CHEMISTRY

TEXTBOOK FOR CLASS XI

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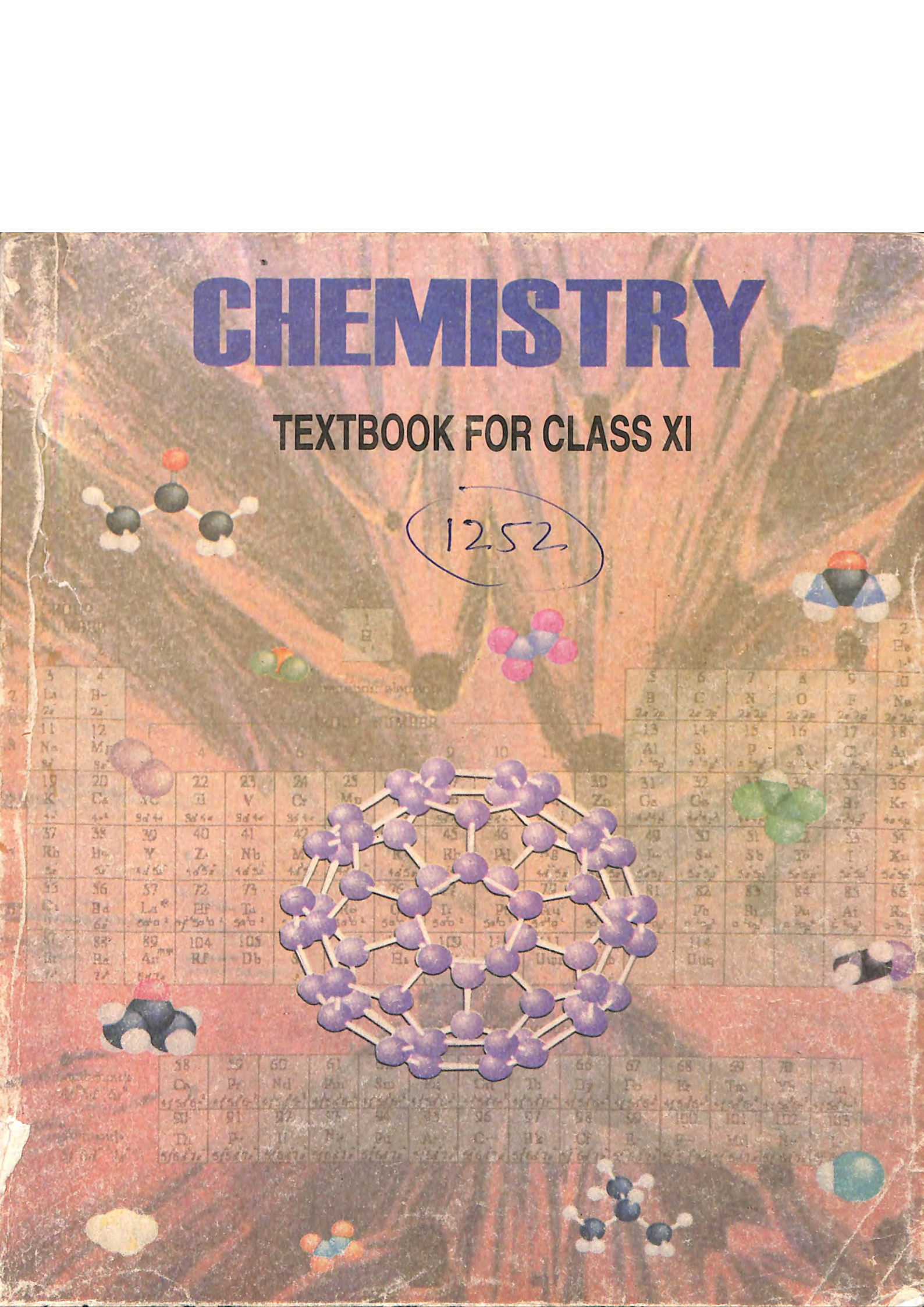

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CHEMISTRY

Textbook for Class XI

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FOREWORD

The National Council of Educational Research and Training (NCERT) has been working for a qualitative improvement of Science and Mathematics education at school level for the last four decades. For this, it has undertaken development of curriculum and curricular materials. By this time, the Council has completed the development of several generation of textual and other related instructional materials with various approaches. These materials are adopted/adapted by States/UTs. All the time, the NCERT's main consideration has been to work strictly according to the National Policy on Education (NPE) and consider various societal and pedagogical issues and concerns during a curriculum renewal process at school level. The National Curriculum Framework for School Education (NCFSE, 2000) brought out by the NCERT is in consonance with these efforts. The NCFSE (2000) reiterated for improving the quality of Science and Mathematics education and teach chemistry as an elective subject at higher secondary stage. The NCFSE also recommends semester-wise development of textual and other related instructional materials. The present Chemistry Textbook for Class XI covers Semesters I and II.

The first draft of the textbook was developed by a team of authors involving experts from the NCERT and various reputed academic and research organisations of the country (given elsewhere). During the development of the present textbook, the writing team considered feedback regarding Chemistry Syllabus and textbooks in vogue. The writing team also took into account the contemporary changes in content and pedagogy which took place during the last decade, in order to make the present book more relevant and meaningful for the students. The draft manuscript was reviewed by a group of experienced practising teachers and subject experts (whose names are acknowledged elsewhere) in a review workshop. The comments/ suggestions received in the review workshop were considered by the authors and draft manuscript was suitably revised. The manuscript was finally edited by a group of experts before its publication.

I am thankful to the Chairman and members of the writing team for their academic contribution at the national level. I am also grateful to the teachers and subject experts of the review workshop for their comments and suggestions, which helped in the refinement of the present book.

The NCERT will welcome suggestions from users of this book for its further improvement.

J.S. RAJPUT
Director
National Council of Educational
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New Delhi
June 2002

PREFACE

The book is written for first introductory separate course in chemistry for those who already have an exposure to an undifferentiated curriculum in general science. The text material has been presented as an appropriate balance between principles, experimental method and factual information. Care has been taken to make the study of concepts and information mutually complimentary instead of overemphasizing one at the cost of the other. The concepts given in the text should help in the organisation, comprehension and explanation of factual information.

The text is designed to cover the academic requirements of Class XI students preparing for higher secondary examination but can also be equally useful for independent study of chemistry at tertiary level or in professional streams. The book is written in a manner to make it self contained, interesting and broad based. Care has been taken to make it easily readable with regard to simplicity of language and clarity of expression. As far as possible we have used SI Units for physio-chemical quantities and IUPAC nomenclature for organic and inorganic compounds. The text carries more than 300 solved examples scattered at strategic places all over the book for better learning of the subject. Historical developments of subject and biographical sketches of eminent chemists have been included to make the book interesting. Each Unit is followed by a large number of exercises for self-testing of the readers for their comprehension and learning of the material covered in the Unit. Some reference material has been given in the form of tables in the text and as appendices at the end of the book. In order to pass on the excitement of modern chemistry to the readers, box material including some advance concepts, new results and important applications has been given at appropriate places in the text.

I am extremely thankful to all the members of the writing team who spared no efforts in writing, revising and finalizing their scripts. I am also thankful to Prof. R.D. Shukla for arranging to redraw all the diagrams and coordinating the activities of the writing team besides overall supervision of its publication.

The best judges of a textbook are its users — the pupils and teachers. It is hoped that the book will live up to their expectations and meet their requirements. We will eagerly await for their comments and suggestions for future improvement of the book. In spite of the considerable care taken in the compilation, editing and printing of the book, some mistakes might have crept in. We seek the indulgence of the readers in this regard and invite them to point out the same.

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UNIT 1

SOME BASIC CONCEPTS OF CHEMISTRY

Objectives

After studying this Unit, you will be able to

- appreciate the importance of chemistry.
- describe the International System of units for measurement of physical quantities and express the result of such measurements to correct significant figures using proper units.
- inter convert unit of measurement and use dimensional analysis correctly in solving problems.
- explain the terms: element, compound, mixture and learn the laws of chemical combination.
- define atomic and molecular masses and describe the *mole* concept and its applications.
- derive the empirical and molecular formula of a compound.
- establish a quantitative relationship between the masses of chemical reactants and the products in a balanced chemical equation (*stoichiometry*).

"Chemistry is the science of molecules and their transformations. It is the science not so much of the one hundred elements but of the infinite variety of molecules that may be ...ilt from them".... ***Roald Hoffmann***

CHEMISTRY deals with the composition, structure and properties of matter. These aspects can be best described and understood in terms of basic constituents of matter: **atoms** and **molecules**. That is why chemistry is called the science of atoms and molecules. Can we see, weigh and perceive these entities? Is it possible to count the number of atoms and molecules in a given mass of matter and have a quantitative relationship between the mass and number of these particles (atoms and molecules)? We will like to answer some of these questions in this Unit. We would further describe how physical properties of matter can be quantitatively described using numerical values with suitable units.

1.1 IMPORTANCE OF CHEMISTRY

Science can be viewed as a continuing human effort to systematize knowledge for describing and understanding nature. For the sake of convenience science is sub-divided into various disciplines : chemistry, physics, biology, geology etc. Chemistry is the branch of science that studies the composition, properties and interaction of matter. Chemists are interested in knowing how chemical transformations occur. Chemistry plays a central role in science and is often intertwined with other branches of science like physics, biology, geology etc. Chemistry also plays an important role in daily life.

Chemical principles are important in diverse areas, such as : weather patterns, functioning of brain and operation of a computer. Chemical industries manufacturing fertilizers, alkalis, acids, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys and other inorganic and organic

chemicals, including new materials, contribute in a big way to the national economy.

Chemistry plays an important role in meeting human needs for food, health care products and other materials aimed at improving the quality of life. This is exemplified by the large scale production of a variety of fertilizers, improved varieties of pesticides and insecticides. Similarly many life saving drugs such as **cisplatin** and **taxol**, efficacious in cancer therapy and AZT (Azidothymidine) used for helping AIDS victims, have been isolated from plant and animal sources or prepared by synthetic methods.

With a better understanding of chemical principles it has now become possible to design and synthesize new materials having specific magnetic, electric and optical properties. This has lead to the production of superconducting ceramics, conducting polymers, optical fibres and large scale miniaturization of solid state devices. In recent years chemistry has tackled with a fair degree of success some of the pressing aspects of environmental degradation. Safer alternatives to environmentally hazardous refrigerants like CFCs (chlorofluorocarbons), responsible for ozone depletion in the stratosphere, have been successfully synthesized. However, many big environmental problems continue to be matters of grave concern to the chemists. One such problem is the management of the Green House gases like methane, carbon dioxide etc. Understanding of bio-chemical processes, use of enzymes for large-scale production of chemicals and synthesis of new exotic materials are some of the intellectual challenges for the future generation of chemists. A developing country like India needs talented and creative chemists for accepting such challenges.

1.2 PHYSICAL QUANTITIES AND THEIR MEASUREMENTS IN CHEMISTRY

Chemists describe, interpret and predict the behaviour of *chemical substances* on the basis of knowledge of their physical and chemical properties determined from careful *experimental measurements*. The measurement of physical properties, unlike that of chemical properties, does not involve any chemical reaction. Properties like mass, length, time, temperature etc., can be quantified and expressed in numerals with suitable units and therefore these are normally called *physical quantities*. As we know every object possesses a certain quantity of matter, called its **mass** (m). The higher the mass an object has, the more difficult is to move it. Thus mass can be determined by measuring resistance to movement. Measurement of mass in chemistry is very important, as chemists are interested to know the quantity of matter. Consequently, a highly accurate mass-measuring device called *analytical balance* is an essential equipment in chemical laboratories. **Length**, **area**, and **volume** measure the size of an object. Length refers to one dimension, area to two dimensions and volume to three dimensions of space. Chemists measure **time** (t) as they want to know how long it takes for a process or a chemical transformation to occur. Some reactions take longer time while others occur in fraction of a second. While conversion of green plants into petroleum takes millions of years, the rusting of iron occurs in hours or days. Precipitation of silver chloride (AgCl) from a solution of silver nitrate ($AgNO_3$), when hydrochloric acid (HCl) is added to it occurs in fraction of a second. Similarly **temperature** is an important physical quantity associated with degree of hotness and coldness. From the operational point of view it determines heat flow from a body at a higher temperature to a body at a lower temperature. Chemists are also interested in temperature changes that occur during chemical reactions.

Length, mass, time and temperature are fundamental physical quantities that we encounter frequently. Amount of a substance (which has direct link with number of atoms and molecules) and the amount of electric charge are also important physical quantities. The meaning of the term *'amount of a substance'* will be discussed in Section 1.7. There are many physical quantities, which we will discuss in other Units of this book. Certain quantities are **derived** with the help of two or more quantities; for example: density is derived from mass and volume.

As already mentioned, all experimental sciences including chemistry, depend on quantitative measurement of properties. Every measurement gives a numerical result that has three aspects: (i) numerical magnitude

(ii) precision, and (iii) indicator of scale, called a unit. All the three aspects must be reported to make a measurement scientifically correct and relevant. Before going to details of numerical magnitude and precision, we will discuss **units** of physical quantities.

1.3 MEASUREMENT AND SI UNITS

The units associated with numerical value of a measurement are as important as the value itself. If the Sun were 149,600,000 metres away rather than 149,600,000 kilometres, the Earth would not be the habitable planet that it is. It is essential to include units with every experimental value. Measurement is the comparison of a physical quantity (to be measured) with a unit of measurement, that is, with a *fixed standard*. The first measurement was probably based on the human body (for example, the length of the foot or hand). Gradually fixed standards developed but these varied from place to place or from country to country. As science became more quantitative in the seventeenth and eighteenth centuries, scientists realized that *standard units* were a necessity. In 1791, a study committee of the **French Academy of Science** devised a system called '*the metric system*' which became a popular system of measurement in the scientific community throughout the world. This was based on decimal system and therefore was convenient to handle as a multiple of ten. It remained in use till 1960.

In 1960,the *General Conference of Weights and Measures* (Conference Generale des Poids et Mesures, CGPM), adopted the **International system of units** (or SI, after the French Le System Internationale Units). This system has seven *SI base units* (Table 1.1). In SI, large and small quantities are expressed by using an appropriate *prefix* (Table 1.2) with the *base units*.

The metre (m) is the SI base unit of length. By combining it with one of the SI prefixes we can get a unit of appropriate size. For instance, national highway distances (distance between two cities) are given in kilometres where 1 kilometre (km) is exactly 1000 or 10^3 metres(m). However, objects in laboratory are often expressed in terms of subdivision of metre, that is as centimetres(cm) or millimetres(mm). The prefix *centi* means 1/100, so centimetre is 1/100 of a metre($1 cm = 1 \times 10^{-2}$ m). Even on a smaller scale, dimensions are measured in nanometre, nm ($1 nm = 1 \times 10^{-9}$ m) or picometre pm, ($1 pm = 1 \times 10^{-12}$ m.) Distance between two atoms in a molecule is normally expressed in picometres. The kilogram(kg) is the SI base unit of mass. This is an unusual base unit in that it contains a prefix. In forming other SI mass units, prefixes are added to the word *gram* (g) to give units such as the milligram ($mg = 10^{-3}$ g)

The second (s) is the SI base unit of time. Combining this unit with prefixes such as milli-, micro-, nano-, and pico-, we can create units of time for measuring very fast changes. For example: some fast chemical reactions take place in nanoseconds and fastest ones in femtoseconds. A modern high-speed computer takes roughly a nanosecond in adding two 10-digit numbers.

Maintaining the National Standards of Measurement

As mentioned above, the system of units (Appendix-A) including unit definitions keeps on changing with time. Whenever the accuracy of measurement of a particular unit was enhanced substantially by adopting new principles, member nations of *metre treaty* (signed in 1875), agreed to change the formal definition of that unit. Each modern industrialized country including India has a National Metrology Institute (NMI) which maintains standards of measurements. This responsibility has been given to the National Physical Laboratory (NPL), New Delhi. This laboratory establishes experiments to realize the *base units* and *derived units* of measurement and maintains National Standards of Measurement. These standards are periodically inter-compared with standards maintained at other National Metrology Institutes in the world as well as those established at the International Bureau of Standards in Paris.

Table 1.1 SI Base Units

Physical Quantity	Name of the Unit	Symbol
Mass	kilogram	kg
Length	metre	m
Time	second	s
Temperature	kelvin	K
Electric Current	ampere	A
Luminous intensity	candela	cd
Amount of substance	mole	mol

Table 1.2 SI Prefixes

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{24}	yotta	Y	10^{-1}	deci	d
10^{21}	zetta	Z	10^{-2}	centi	c
10^{18}	exa	E	10^{-3}	milli	m
10^{15}	peta	P	10^{-6}	micro	μ
10^{12}	tera	T	10^{-9}	nano	n
10^{9}	giga	G	10^{-12}	pico	p
10^{6}	mega	M	10^{-15}	femto	f
10^{3}	kilo	k	10^{-18}	atto	a
10^{2}	hecto	h	10^{-21}	zepto	z
10	deca	da	10^{-24}	yocto	y

1.3.1 Derived Units

There are many physical quantities in chemistry which are measured in the laboratory. Their units are obtained using SI base units. Here it would be relevant to mention that we multiply and divide the symbols for units as if they were algebraic quantities. For example, the result of dividing 10 g by 5 g is a pure number with no units, because the units (grams) cancel out.

$$\frac{10\,\cancel{g}}{5\,\cancel{g}} = \frac{10}{5} = 2$$

To determine the volume of a box of sides 1.0 m, 2.0 m, and 2.5 m, we multiply its height, breadth and length to get the volume

Volume = (1.0 m) × (2.0 m) × (2.5 m) = 5.0 m^3

The result is short hand for 5.0 × (1m^3), where m^3 is SI unit of volume. Units built up in this way are called ***derived units***. We generally, report the volumes of liquids and gases in litre (L), where 1L is exactly 1000 cm^3 or 1 dm^3.

The density of a substance is defined by

$$\text{density} = \frac{\text{mass of sample}}{\text{volume of sample}}$$

The SI unit of density is found by dividing the SI unit of mass by the SI unit of volume

$$\text{Unit of density} = \frac{1\text{ kg}}{1\text{ m}^3} = 1\text{ kg m}^{-3}$$

Density is an example of an **intensive property,** *a property that is independent of the size of the sample, Properties that depend on the size of the sample*, like mass, and volume are called **extensive properties**.

Sometimes the unit kg/m^3 or kg m^{-3} is not convenient and we use gram/centimetre^3 or g cm^{-3} (1g cm^{-3} = 10^3 kg m^{-3}). Similar to volume and density, units for other quantities are built up from base units. Thus units of physical quantities like **energy**, **work**, **heat**, **electric charge** etc. are based on SI base units. However some of these units are named after scientists who did pioneering work in the related fields. For example, the unit of energy is 'joule' abbreviated as 'J'; the unit of electric charge 'coulomb' is abbreviated as 'C'. The symbols of units, which bear the names of the scientists, are normally written in capital letters. For example, the unit 'joule' adopted after the name of James P. Joule is denoted by 'J' (capital J). A few selected derived units are given in Table 1.3.

Table 1.3 Derived Units

Quantity	Definition of Quantity	Expression in terms of SI base units
Area	Length squared	m^2
Volume	Length cubed	m^3
Density	Mass per unit volume	kg/m^3 or $kg\ m^{-3}$
Velocity	Distance traveled per unit time	m/s or ms^{-1}
Acceleration	Velocity changed per unit time	m/s^2 or ms^{-2}
Force	Mass times acceleration of object	$kg.m/s^2$ or $kg\ ms^{-2}$(newton,N)
Pressure	Force per unit area	$kg/(m.s^2)$ or $kg\ m^{-1}s^{-2}$(Pascal, Pa)
Energy (work, heat)	Force times distance travelled	$kg\ m^2/s^2$ or $kg\ m^2s^{-2}$(joule,J)
Electric charge	Ampere times second	A s (coulomb,C)
Electric potential	Energy per unit charge	J/(A s) potential difference (volt,V)

REFERENCE STANDARD

After defining a unit of measurement such as the kilogram or the metre, scientists agreed on reference standards that make it possible to calibrate all measuring devices. For getting reliable measurements, all devices as *metre sticks* and *analytical balances* have been calibrated by their manufacturers to give correct readings. However, each of these devices is standardized or calibrated against some reference. The mass standard is the kilogram since 1889. It has been defined as the mass of platinum-iridium (Pt-Ir) cylinder that is stored in an airtight jar at International Bureau of Weights and Measures in Sevres, France. Pt-Ir was chosen for this standard because it is highly resistant to chemical attack and its mass will not change for an extremely long time.

Scientists are in search of a new standard for mass. This is being attempted through accurate determination of Avogadro's constant. Work on this new standard focuses on ways to measure accurately the number of atoms in a well-defined mass of sample. One such method, which uses x-rays to determine the atomic density of a crystal of ultrapure silicon, has an accuracy of about 1 part in 10^6 but has not yet been adopted to serve as a standard. There are other methods but none of them are presently adequate to replace the Pt-Ir cylinder. No doubt, changes are expected within this decade.

The metre was originally defined as the length between two marks on a Pt-Ir bar kept at a temperature of 0°C (273K). In 1960 the length of the metre was defined as 1.65076373×10^6 times the wavelength of light emitted by a krypton laser. Although this was a cumbersome number, it preserved the length of the metre at its agreed value. The metre was redefined in 1983 by CGPM as the length of path travelled by light in vacuum during a time interval of 1/299 792 458 of a second. Similar to length and mass, there are reference standards for other physical quantities.

1.4 MEASUREMENT AND SIGNIFICANT FIGURES

1.4.1 Precision and Accuracy

One of the reasons for the high credibility of scientists is the honesty with which they have to report measurements. Every measurement is limited by the *reliability of the measuring instrument and the skill of the person making the measurement.* In each measurement *uncertainty* should be reported correctly.

If we repeat a particular measurement, we usually do not obtain precisely the same result as each measurement is subject to experimental error. Different measured values vary slightly from one another. *The term* ***precision*** *refers for the closeness of the set of values obtained from identical measurements of a quantity.* **Accuracy**, a related term, *refers to the closeness of a single measurement to its true value.* Let us take an example to illustrate it. Three students were asked to determine

Table 1.4 Data to Illustrate Precision and Accuracy

	Measurements/g			
	1	2	3	Average (g)
Student A	0.521	0.515	0.509	0.515
Student B	0.516	0.515	0.514	0.515
Student C	0.521	0.520	0.520	0.520

the mass of a piece of metal where mass is known to be 0.520g. Data obtained by each student are recorded in Table 1.4.

The data for student A are neither very precise nor accurate; the individual values differ widely from one another and average value is not accurate. Student B was able to determine the mass of the metal more precisely. The values deviate but little from one another, however the average mass is still not accurate. In contrast, the data for student C is both precise and accurate.

1.4.2 Scientific (Exponential) Notation

Very large and very small numbers are common in chemistry. Repeatedly writing down such numbers in the ordinary way (as in the case of the Avogadro constant 602,213,700 000 000 000 000 000) would be tedious and inevitably result in errors. A better way to represent such numbers is essential for a convenient and accurate manipulation. Scientific notation offers such a way.

In **scientific notation**, all numbers, however, large or small, are expressed as a number between 1.000... and 9.999... multiplied or divided by 10,an appropriate number of times. For example,

$$138.42 = 1.3842 \times 10 \times 10 = 1.3842 \times 10^2$$

Here 2 is the power or exponent, to which 10 is raised.

In scientific notation, a number is generally expressed in the form

$$N \times 10^n$$

where N is a number (called **digit term**) between 1.000..... and 9.999..... and n is a number (not necessarily a single digit) called an ***exponent***. To express a number smaller than 1.000....in scientific notation, the appropriate number between 1.000... and 9.999... is divided by 10 an appropriate number of times.

For example,

$$0.00013842 = \frac{1.3842}{10 \times 10 \times 10 \times 10} = 1.3842 \times 10^{-4}$$

To transform a number larger than 9.999.. to scientific notation, the decimal point is moved to the left until there is only one non-zero digit before the decimal point. If the decimal point is moved x places to the left, the exponent n = x. Thus in transforming 138.42 to scientific notation the decimal point is moved to the left two places. So exponent n=2 and we can write.

$$138.42 = 1.3842 \times 10^2$$

To transform a number smaller than 1.000... to scientific notation, the decimal point is moved to the right until there is one non-zero digit before the decimal point. If the decimal point is moved y places to the right, the exponent n = -y. For example, when 0.00013842 is to be transformed to scientific notation, decimal point is moved **four** places to the right.

So the exponent n = -4 and we can write

$$0.00013842 = 1.3842 \times 10^{-4}$$

To add or subtract numbers in scientific notation, the power of 10, that is, the exponent, n must be the same in both the numbers. For example, we have to add 6.234×10^4 and 1.203×10^3. We have to transform 1.203×10^3 to 0.1203×10^4 and then add

$$6.234 \times 10^4 + 0.1203 \times 10^4$$

$$= (6.234 + 0.1203) \times 10^4 = 6.3543 \times 10^4$$

To multiply two numbers in scientific notation we make use of the relation

$$(10)^x \ (10)^y = 10^{(x+y)}$$

For example,

$$(3.025 \times 10^3)\ (6.217 \times 10^{-6}) = 18.81 \times 10^{3-6}$$

$$= 18.81 \times 10^{-3} = 1.881 \times 10^{-2}$$

To divide two numbers in scientific notation we make use of the relation

$$\frac{10^x}{10^y} = 10^{x-y}$$

For example,

$$\frac{3.81\times10^{12}}{6.22\times10^{23}} = \frac{3.81}{6.22}\times10^{(12-23)} = 0.613\times10^{-11} = 6.13\times10^{-12}$$

1.4.3 Significant Figures

In the laboratory we have to worry about obtaining results that are reliable. Some of the data we collect are more precise than others. It is common sense that the answer to a calculated quantity can be known no more precisely than the least precise piece of information. This is where the concept of *significant figures* or *significant digits* comes in handy.

Every measurement (other than counting such as 10 beakers, 13 test tubes) gives an *inexact number* because every such measurement is uncertain to some extent. For example, distance between two cities is reported as certain number of kilometres from each other. Another example: the mass of a metal piece can be determined with greater precision in an analytical balance than with a platform balance (Table 1.5).

Table 1.5

	Platform balance	Analytical balance
Measured quantity	10.3 g	10.3106 g
Uncertainty	± 0.1 g	± 0.0001 g
Mass	10.3 ± 0.1g	10.3106 ± 0.0001g
Precision	low	high

Here, we have recorded the mass as 10.3 ± 0.1g or 10.3106 ± 0.0001g and normally this notation should be adopted although it is a bit cumbersome. Therefore, an alternative approach is adopted by scientists in which it is assumed that when a number is written down, all the digits preceding the last one are known with certainty and that there is an uncertainty of about one unit in the last digit. Thus the number 10.3 is between 10.2 and 10.4 whereas number 10.3106 is between 10.3105 and 10.3107. The number 10.3 is said to consist of three significant figures whereas 10.3106 consists of six significant figures. Thus precision of a measurement is indicated by the number of figures used to record it. *The digits in a properly recorded measurement are known as* ***significant figures***. Alternatively, significant figures are the meaningful digits in a measured or calculated quantity. The precision of a measurement depends upon the limitations of the measuring device and skills with which it is used as mentioned earlier. A significant figure includes all those digits that are known with certainty plus one more which is estimated or is uncertain. Therefore while reporting a particular result in laboratory one should not report more precisely than desirable as mentioned earlier. *The greater the number of significant figures in a reported result, smaller is the uncertainty and greater the precision.*

Determining the significant figures in numbers 1.007, 12.012 and 10.070 is not difficult. They are 4, 5 and 5 respectively. But what about numbers like 20.000 and 0.00002? Do these have five significant figures? Here, it is quite interesting while first one has five significant figures, the second one i.e. 0.00002 has only 'one'. The four zeros preceding the significant digit '2' are written simply to locate the decimal point. Contrary to this, another number 0.000020 has two significant figures as the final zero is not needed to locate the decimal point. It is a part of the measured quantity. Zeros that arise as a part of a measurement, are significant. For example: 106.540 has 6 significant figures, 0.0005030 has 4 significant figures and 6.02×10^{23} has 3 significant figures.

1.4.4 Guidelines for Determining Significant Figures

Rule 1: To determine the number of significant figures in a measurement, read the number from left to right and count all the digits, starting with the first digit that is not zero.

Example	Number of significant figures
1.23g	Three
0.00134 g	Three; The zeros to the left of 1 simply locate the decimal point. For avoiding confusion, write number of this type in scientific notation; thus $0.00134\ g = 1.34 \times 10^{-3}\ g$
3.0 g and 0.030 g	Two; Both of these numbers have two significant digits. When a number is greater than1, *all the zeros to the right of the decimal point are significant.* For a number less than 1, only zeros to the right of the first significant digit are significant.
100 g	In numbers that do not contain a decimal point, "trailing"zeros may or may not be significant. If only the last digit is uncertain there are 3 significant figures. Therefore it is suggested that number should be written in a scientific notation as 1.00×10^2. Alternatively, this idea can be conveyed by following the number with a decimal point (100.). This practice will be normally followed in this book and finally 1×10^2 would imply only one significant figure. Thus it can be seen that for a number written in scientific notation all digits are significant.
π=3.1415926	The value for π is known to a large number of significant figures: one may choose the number of digits appropriate to one's calculation.

Rule 2: When adding or subtracting, the number of decimal places in the answer should be equal to the number of decimal places in the number with the *fewest* places. For example :

0.13	2 significant figures	2 decimal places
1.5	2 significant figures	1 decimal place
20.911	5 significant figures	3 decimal places
22.541		

Since the term, 1.5 involved in addition, has only one decimal place, the overall answer of 22.541 should be reported as 22.5.

Rule 3: In multiplication and division, the number of significant figures in the answer should be the same as that in the quantity with the *least number of* significant figures. Thus in

$$\frac{0.01208}{0.0236} = 0.512$$

or, in exponential notation, 5.12×10^{-1}. The number 0.0236 has only three significant figures; the answer must also be limited to three significant figures as reported above.

Similarly, the product $152.06\times 0.24 = 36.4944$ should be reported as 36 because number, 0.24 has only two significant figures.

Rule 4: When a number is *rounded off* the number of significant figures is reduced, the last digit retained is increased by 1 only if the following digit is ≥ 5, and is left as such if the following digit is ≤ 4. For example: 12.696, 18.35 and 13.93 are as 12.7, 18.4 and 13.9 respectively when rounded off to three significant figures.

While solving problems all significant digits used in calculation should be taken up and only the final result should be rounded off to the desirable number of significant digits.

1.5 UNITS AND DIMENSIONAL ANALYSIS

1.5.1 Conversion of Units

We shall be using mostly SI units for physical quantities in this book. If for all the physical quantities we use SI base or derived units in our calculations then the final physical quantity obtained in the result will always have the appropriate SI units. This *coherence* is a great advantage in using the SI units. On many occasions we are required to convert one set of units into other units that may or may not be SI units. For example, distance reported in miles, bond length reported in Angstrom (Å) and weight reported in pounds represent non-SI units and a convenient way of their conversions is the **unit factor method**. In order to use this method, we write the units with every number and carry the units through the calculation, treating them as algebraic quantities. For

nterconversion of the units of time (minutes nd seconds) we know the basic relationship, min = 60s which may be written as:

$$1 = \frac{60\ \text{s}}{1\ \text{min}} \quad \text{or} \quad 1 = \frac{1\ \text{min}}{60\ \text{s}}$$

These equalities are called *unit conversion factors*, or *conversion factors* or simply *unit factors* because the overall effect of multiplication by these factors is to multiply by 1. Therefore, multiplication of an original quantity by this factor does not change the magnitude of that quantity, only its numerical value and units are changed. For example to find the number of seconds in 5.0 min , we write

$$5.0\,\text{min} = (5.0\,\cancel{\text{min}})\left(\frac{60\,\text{s}}{1\,\cancel{\text{min}}}\right) = 300\,\text{s}$$

We cancel the unit 'minutes' and the result is then the same quantity expressed in seconds. It may be emphasized that the magnitude of time expressed either as 5 minutes or 300 seconds remains unaltered. Similarly, Angstroms and picometres can be interconverted using the equations.

We know, $1\,\text{Å} = 10^{-10}\,\text{m}$

or unit factor, $1 = \frac{10^{-10}\,\text{m}}{1\,\text{Å}}$

Suppose we have to convert 0.74 Å into picometre, We write,

$$0.74\,\text{Å} = 0.74\,\cancel{\text{Å}}\left(\frac{10^{-10}\,\text{m}}{1\,\cancel{\text{Å}}}\right) = 0.74\times10^{-10}\,\text{m}$$

Further, $1\text{pm} = 10^{-12}\,\text{m}$ or $1 = \frac{1\text{pm}}{10^{-12}\,\text{m}}$

Therefore, $0.74\times10^{-10}\,\text{m}$

$$= 0.74\times10^{-10}\,\cancel{\text{m}}\left(\frac{1\text{pm}}{10^{-12}\,\cancel{\text{m}}}\right) = 74\ \text{pm}$$

We can also write this conversion in one step by multiplying with two successive *unit factors* as shown below:

$$0.74\ \text{Å} = 0.74\,\cancel{\text{Å}}\times\frac{10^{-10}\,\cancel{\text{m}}}{1\,\cancel{\text{Å}}}\left(\frac{1\text{pm}}{10^{-12}\,\cancel{\text{m}}}\right) = 74\ \text{pm}$$

Another interesting example is the conversion of litre-atmosphere to joule (the SI unit of energy) by multiplying with two successive unit factors. Thus,

$$1\,\text{L atm}\times\left(\frac{10^{-3}\,\text{m}^3}{1\text{L}}\right)\times\frac{101{,}325\,\text{Pa}}{1\text{atm}} = 101.325\,\text{Pa m}^3$$

Knowing that $\text{Pa} = \frac{\text{N}}{\text{m}^2}$, we can write

$$101.325\,\text{Pa m}^3 = 101.325\left(\frac{\text{N}}{\text{m}^2}\right)\text{m}^3$$

$$= 101.325\,\text{N m} = 101.325\,\text{J}$$

Hence 1 L atm = 101.325 J

1.5.2 Problem Solving Using Dimensional Analysis

Dimensional analysis is a systematic way of solving numerical problems. Every physical quantity must be represented by a number with some units and in any calculation if these are manipulated correctly, the final result appears as a number with appropriate units. If we solve the problem incorrectly, the final quantity will not have correct units and we know immediately that we have made a mistake. The method is such a valuable tool that it is worthwhile to illustrate it by the following example

Example 1.1

What is the mass of 1 L of mercury in grams and in kilograms if the density of liquid mercury is 13.6 g cm^{-3}?

Solution

We know the relationship, 1L = 1000 cm^3 and also, $\text{density} = \frac{\text{mass}}{\text{volume}}$

We can write, mass = (volume) (density)

Therefore, the *mass of 1L of mercury* is equal to

$$(1\text{L})\left(\frac{1000\ \text{cm}^3}{1\text{L}}\right)(13.6\text{g cm}^{-3})$$

$$= (1000\ \text{cm}^3)\ (13.6\ \text{g cm}^{-3}) = 1.36\text{x}10^4\ \text{g}$$

The mass in kilograms can be calculated as

$$1.36\times10^{4}\,g=(1.36\times10^{4}\,g)\left(\frac{1\,kg}{1000\,g}\right)=13.6\,kg$$

(Remember, $\frac{1000\,cm^3}{1\,L}$ and $\frac{1\,kg}{1000\,g}$ are *conversion factors* with which we have to multiply for getting our answer in appropriate units.)

1.6 MATTER

You are familiar from your studies in secondary classes that anything which has mass and occupies space is *matter*. All the things around you, e.g. water, air, book, table etc. are matter. *Material* is another very common term used in chemistry. However this word has a limited meaning, which corresponds to matter having specific use(s). For example cement, glass, wood, paper etc. are matter but also termed as materials on account of their specific uses.

Solid, liquid and gaseous states represent three different states of aggregation and provide a basis of the physical classification of matter. Gaseous state of matter at very high temperatures containing gaseous ions and free electrons is referred to as the *plasma state*. Description of matter merely in terms of states of aggregation does not suffice and it becomes necessary to make use of other properties to obtain a more useful classification of matter. One such useful way studied by you at the secondary stage, is to classify matter into the categories: *elements, compounds* and *mixtures*. Some of their characteristics are illustrated in Fig.1.1.

Let us see how this scheme simplifies the study of chemistry.

An element consists of only one kind of atoms. Molecules are identifiable units of matter consisting of two or more atoms of the same element or of different elements combined in a definite ratio. Mono, di, or polyatomic molecules or extended structures with the same kind of

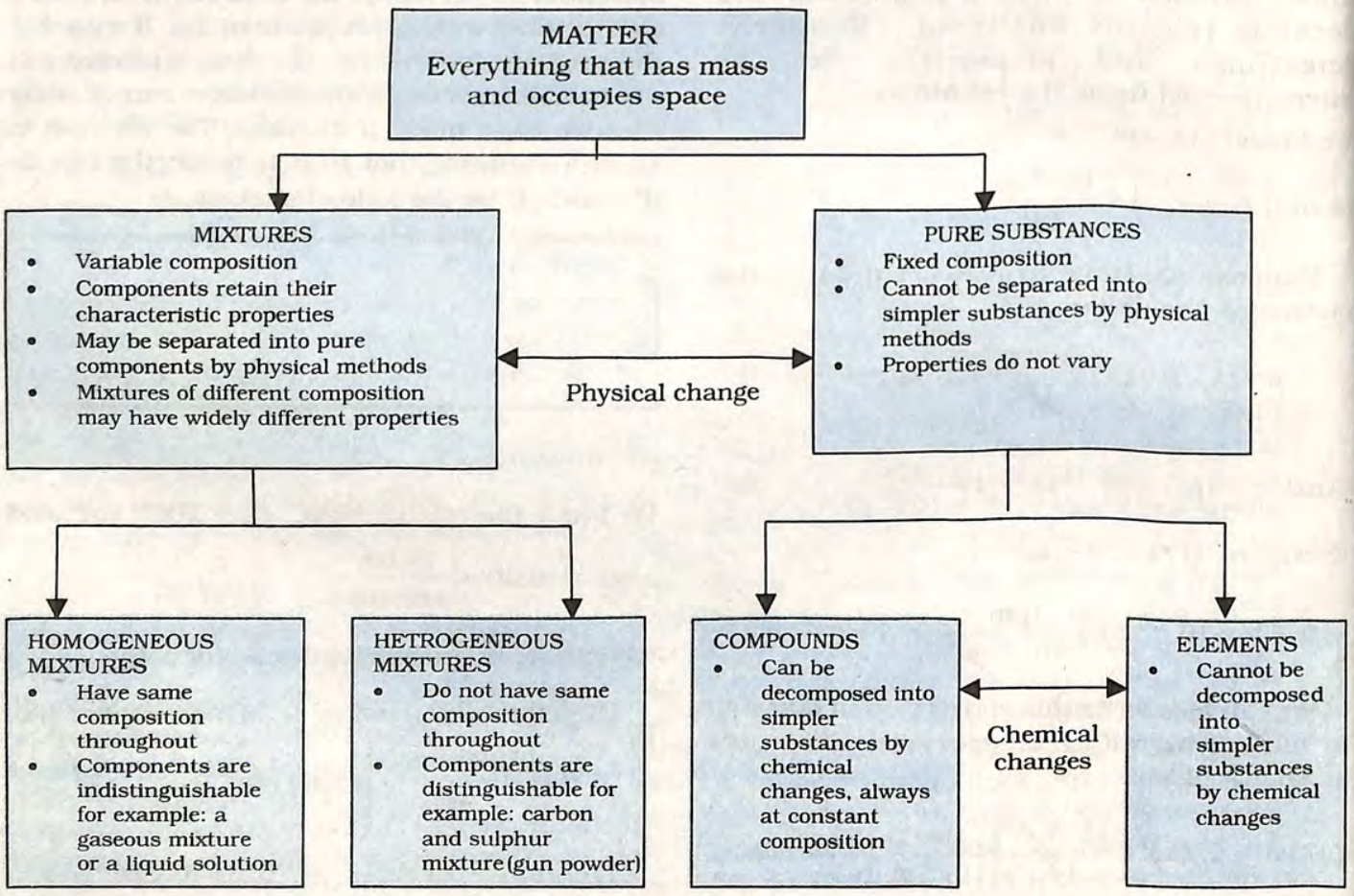

MATTER
Everything that has mass and occupies space
MIXTURES
Variable composition
Components retain their characteristic properties
May be separated into pure components by physical methods
Mixtures of different composition may have widely different properties
Physical change
PURE SUBSTANCES
Fixed composition
Cannot be separated into simpler substances by physical methods
Properties do not vary
HOMOGENEOUS MIXTURES
Have same composition throughout
Components are indistinguishable for example: a gaseous mixture or a liquid solution
HETROGENEOUS MIXTURES
Do not have same composition throughout
Components are distinguishable for example: carbon and sulphur mixture (gun powder)
COMPOUNDS
Can be decomposed into simpler substances by chemical changes, always at constant composition
Chemical changes
ELEMENTS
Cannot be decomposed into simpler substances by chemical changes

Fig 1.1 *A scheme of classification of matter.*

atoms constitute elements while in a compound two or more than two different types of atoms are present (sugar, salt, water are examples). A compound is quite different from a mixture. Elements in a compound lose their individual chemical characteristics. Hydrogen and oxygen which are gases at room temperature lose their chemical identity when they form water whose properties are different from its constituents. In a mixture, each of the constituents retains its characteristic properties, e.g. sugar retains its characteristic sweetness even in its aqueous solution. A mixture, to a large extent, shows the combined behaviour of the substances present in it.

A mixture may be *homogeneous* or *heterogeneous*. A homogeneous mixture has the same composition throughout. If you stir, sugar in a glass of water, sugar molecules get distributed uniformly, i.e. there is homogeneity throughout the mixture. This is an example of a *homogeneous mixture*. It can have two or more components. In contrast, a mixture of grains of sand and salt is heterogeneous, since particles of each component of the mixture remain separate and can be observed as individual grains under a microscope.

1.7 THE MOLE CONCEPT

We know that when a certain number of atoms or molecules of one element react with a definite number of atoms or molecules of another, a new compound is formed. In view of the quantitative nature of chemistry one would like to know the number of atoms or molecules of each element used in a particular reaction. This means that there must be some method of counting these entities, no matter how small they are. The solution to this problem is to have a convenient unit of matter that contains a known number of *entities*. The search has led to the adoption of **mole as the chemical counting unit**.

> The word 'mole' was introduced around 1896 by Wilhelm Ostwald who derived the term from Latin word *moles* meaning a 'heap' or 'pile'. A substance may be considered as a heap of atoms or molecules. The unit 'mole', in 1967, was accepted to provide a simple way of reporting a large number – the massive heap of atoms and molecules in a sample.

In SI Units we represent mole by the symbol 'mol' (Section 1.3). It is defined as follows:

A mole is the amount of a substance that contains as many entities (atoms, molecules or other particles) as there are atoms in exactly 0.012 kg (or 12 g) of the carbon-12 isotope.

It may be emphasised that the mole of a substance always contains the same number of entities, no matter what the substance may be. In order to determine this number precisely, the mass of a carbon-12 atom was determined by a mass spectrometer and found to be equal to 1.992648×10^{-23} g. Knowing that 1 mol of carbon weighs 12g, the number of atoms in it is equal to:

$$\frac{12\,\text{g/mol}\ ^{12}\text{C}}{1.992648 \times 10^{-23}\ \text{g}\ /\ ^{12}\text{C atom}}$$

$$= 6.022137 \times 10^{23}\ \text{atoms/mol}$$

In a simple way, we can say that mole has 6.022137×10^{23} entities (atom, molecules or ions etc).

The number of entities in 1 mol is so important that it is given a separate name and symbol, known as ***'Avogadro Constant'*** denoted by N_A in honour of the nineteenth century Italian scientist, Amedeo Avogadro. Though this quantity is known to seven significant figures, in most calculations the value, 6.022×10^{23} entities/mol for N_A is generally used.

Here entities may represent atoms, ions, molecules or other subatomic entities. A mole is a convenient unit for expressing the *amount of a substance*. Just as eggs and bananas are counted by the dozen, paper by the **ream**, similarly, the mole is the counting unit used by chemists for 6.022×10^{23} particles of a substance (element or compound).

1 mol of hydrogen contains 6.022×10^{23} hydrogen molecules, 1 mol of sodium contains 6.022×10^{23} sodium atoms and 1 mol of ethyl alcohol (C_2H_5OH) contains 6.022×10^{23} molecules of ethyl alcohol. We have just seen that 6.022×10^{23} atoms of carbon-12 weigh 12g. Similarly one mole of H_2, sodium and ethyl alcohol weigh 2.0 g, 23.0 g and 46.0 g respectively. This relationship between number of particles (atoms, molecules, ions etc) and their masses has proved very meaningful. *Chemists count the number of atoms and molecules by*

weighing. In a reaction we require these particles (atoms, molecules and ions) in a definite ratio. We make use of this relationship between numbers and masses of the particles for determining the stoichiometry of reactions (Sections 1.12 and 1.13).

A mole contains a huge number of particles. Obviously, the mole is not a useful measure for things much larger than atoms and molecules in size or mass. For example, one mole of glass marbles would be sufficient to cover the earth with a 5 km thick layer. Being a SI unit, mole can be used with a prefix. For example, 1 mmol, 1 μmol and 1 nmol are equal to 10^{-3} mol, 10^{-6} mol and 10^{-9} mol respectively. We convert number of entities/particles into mole and vice versa using Avogadro constant. Suppose a sample of vitamin C is known to contain 1.29×10^{24} hydrogen atoms. We express this number as the number of moles of hydrogen atoms as follows:

$$\text{Number of moles of H atoms} = \frac{\text{Number of H atoms}}{N_A}$$

$$\frac{1.29\times10^{24}\ \text{atoms}}{6.022\times10^{23}\ \text{atoms mol}^{-1}} = 2.14\ \text{mol}$$

($N_A = 6.022 \times 10^{23}$ atoms / mol)

Here, it is much simpler to report that 2.14 mol of hydrogen atom are present rather than saying 1.29×10^{24} atoms of hydrogen.

It is obvious that, one mole molecules of ammonia (NH_3) contain one mole of nitrogen atoms and three mole of hydrogen atoms. Similarly one mole of glucose *molecules* ($C_6H_{12}O_6$) contains six moles of carbon atoms, twelve moles of hydrogen atoms and six moles of oxygen atoms. It has already been mentioned that 1 mole of different substances have different masses. Fig.1.2(a) and 1.2(b) depict 1 mol of some elements and 1 mol of some compounds respectively,

1.8 LAWS OF CHEMICAL COMBINATION

The great French chemist, Antoine Laurent Lavoisier (1743-1794) established that *matter can neither be created nor destroyed in a chemical reaction.* This historical finding put chemistry on a firm footing. In fact, this was the result of exact measurement of masses of reactants and products, and carefully planned

Fig.1.2(a) *Each sample consists of 1 mol of atoms of the element. Mass of one mole of each element is shown after its name in parenthesis Clockwise from left: copper (63.5 g), sulphur (32 g), iodine (127 g), iron (56 g), carbon (12 g) and (in centre) mercury (200.5 g)*

Fig.1.2(b) *One mole sample of compounds. Mass of one mole of each compound is shown in parenthesis after its name. (clockwise from top) copper sulphate pentahydrate $CuSO_4$ $5H_2O$ (249.5 g), water, H_2O (18 g), sodium chloride, NaCl (58.5 g), glucose $C_6H_{12}O_6$ (180 g), potassium dichromate $K_2Cr_2O_7$ (294 g) and (in centre) sucrose $C_{12}H_{22}O_{11}$ (342 g)*

experiments performed by Lavoisier.

The law of conservation of mass helped in establishing the *law of constant composition* or *law of definite proportions*. This law states that a *sample of a pure compound whatever its source, always consists of the same elements combined in the same proportions by mass.* For example, one molecule of ammonia always has the formula NH_3. That is one molecule of ammonia always contains one atom of nitrogen and three atoms of hydrogen or 17.0 g of ammonia always contain 14.0 g of nitrogen and 3.0 g of hydrogen. Thus, nitrogen and hydrogen

will react in the ratio of 14 : 3 by mass. We have just seen that there are two equivalent ways to express molecular composition (i) in terms of number of atoms of each type per molecule and (ii) in terms of masses of elements per mole.

John Dalton observed that an element may form more than one compound with another element. He noted that for a given mass of an element, the masses of the other element in two or more compounds are in the ratio of small integers. This is known as the **law of multiple proportions**. This observation led to formulation of his *'Atomic Theory'* (Section 1.9). In ammonia we have seen that 3 mol of H (3.0 g) combine with 1 mol of N (14.0 g) while in hydrazine (N_2H_4), 4 mol of H combine with 2 mol of N.

It can be seen that for 14.0 g of N we require 3.0 g of H in NH_3 and 2.0 g H in N_2H_4 leading to the ratio

$$\frac{\text{3.0g H per 14.0g N in } NH_3}{\text{2.0g H per 14.0 N in } N_2H_4} = 3/2$$

That is, masses of hydrogen which combine with the fixed mass of nitrogen are in a simple ratio of 3:2. This is in agreement with the *law of multiple proportions*.

1.8.1 Gay-Lussac's Law and Avogadro's Law

The French chemist, Gay Lussac experimented with the reaction of gases and found that *the volume of reactants and products in a large number of chemical reactions are related to each other by small integers, provided the volumes are measured at the same temperature and pressure.* For example, in the reaction of hydrogen with oxygen to produce water vapour, it was found that two volumes of hydrogen and one volume of oxygen give two volumes of water vapour. This means that 100 mL of H_2 gas will combine exactly with 50 mL of O_2 gas to give exactly 100 mL of H_2O vapour if all the gases are measured at the same temperature and pressure (say 100°C and 1 atm pressure).

Gay-Lussac's discovery of integer ratio in volume relationship is actually the ***law of definite proportions by volume***. The law of definite proportions, stated earlier, was with respect to mass. The Gay-Lussac's law, which was based on experimental observation, was explained properly by the work of Italian physicist and lawyer Amedeo Avogadro in 1811.

Avogadro's law states that:

The volume of a gas (at fixed pressure and temperature) is proportional to the number of moles (or molecules of gas present). Mathematically we can write

$$V \propto n$$

(where n is the number of moles of gas). Avogadro's law can be stated in another simple way: *equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.*

Both the Gay-Lussac and Avogadro laws can be illustrated as follows:

Gay-Lussac's law	$2H_2(g)$ +	$O_2(g)$ →	$2H_2O(g)$
	2 volume	1 volume	2 volume
Avogadro's law	2 mol of H_2 +	1 mol of O_2 →	2 mol of H_2O
	$2 \times 6.022 \times 10^{23}$ molecules of H_2	$1 \times 6.022 \times 10^{23}$ molecules of O_2	$2 \times 6.022 \times 10^{23}$ molecules of H_2O

1.9 DALTON'S ATOMIC THEORY

John Dalton, in 1803, proposed the **Atomic Theory of Matter** on the basis of laws of chemical combination and other related chemical observations. He stated that :

- all matter is made of atoms which are indivisible and indestructible ultimate particles.
- all the atoms of a given element are identical, both in mass and chemical properties. However, atoms of different elements have different masses and different chemical properties.
- compounds are formed by the combination of different atoms in the ratio of small whole numbers.
- chemical reactions involve only combination, separation or rearrangement of atoms.
- atoms are neither created nor destroyed in the course of an ordinary chemical reaction.

Even today, the scientific community accepts the hypothesis of John Dalton with two modifications: (i) an atom is 'divisible and destructible, and (ii) all atoms of an element are not identical in mass. However, these aspects have not affected the basic philosophy of Dalton.

1.10 ATOMIC, MOLECULAR AND MOLAR MASSES

Dalton gave the idea of atomic mass in relative

terms, that is, the average mass of one atom relative to the average mass of the other. The relative atomic masses were referred to as the **atomic weights**. It was found that 1.00 g of hydrogen combines with 8.0 g of oxygen to form water. In order to find out atomic mass of oxygen (relative to hydrogen) we need to know the relative numbers of hydrogen and oxygen atoms in water. However during Dalton's time it was not known how many hydrogen and oxygen atoms are present in a water molecule. Now we know that a water molecule has two hydrogen and one oxygen atom. So, atomic mass of oxygen on the hydrogen scale is given by

$$\frac{\text{Relative mass of one atom of oxygen}}{\text{Relative mass of one atom of hydrogen}} = 2 \times 8 = 16$$

Thus the atomic mass of oxygen relative to hydrogen is 16.

Dalton's hydrogen based scale was eventually replaced by a scale based on oxygen, as it was considered more reactive forming a large number of compounds. For a universally accepted atomic mass unit in 1961, *carbon-12 isotope was selected as standard.* Today this *scale* depends on measurements of atomic mass by a **mass spectrometer**. We can make accurate measurements of mass on this instrument by comparing mass of an atom with the mass of a particular atom chosen as standard. On the present atomic mass scale, the carbon-12 isotope is chosen as the standard and is arbitrarily assigned a mass of exactly 12 atomic mass unit. One atomic mass unit (amu) is therefore, a mass unit equal to exactly one-twelfth the mass of a carbon-12 atom. However, the new symbol used is 'u' (unified mass) in place of amu.

It would be relevant to mention here that a particular element may consist of several isotopes with different atomic masses. The average relative atomic mass depends upon the isotopic composition of that particular element. The mass spectrum provides information regarding the masses of the isotopes and their relative abundance required for calculation of the average relative atomic masses. *The **fractional abundance** of an isotope is the fraction of the total number of atoms that is composed of that particular isotope.*

Let us take an example of neon to illustrate this. In naturally occurring neon, isotopes and their relative abundance are as follows :

Isotope	Fractional Abundance
^{20}Ne	0.9051
^{21}Ne	0.0027
^{22}Ne	0.0922

Average atomic mass of Ne = $20 \times 0.9051 + 21 \times 0.0027 + 22 \times 0.0922 = 20.179$ u

The *relative molecular mass* or the *relative formula mass* (in the case of ionic substances) is the sum of the relative atomic masses of the constituent atoms. This is normally done when molecular formula is known. For example, molecular formula of ammonia is NH_3, therefore, its molecular mass is

(1×14.0 u) for 1 nitrogen atom + (3 × 1.0 u) for 3 hydrogen atoms = 17.0 u

*The **formula mass** of a substance is the sum of the atomic masses of all atoms in a formula unit of the compound.* Sodium chloride, NaCl is an ionic substance and we do not talk about its molecular mass. Formula mass of NaCl = 58.5 u (for Na = 23.0 u and Cl = 35.5 u).

1.10.1 Molar Mass and Molar Volume

We have studied in Section 1.7 that 1 mol consists of 6.022×10^{23} entities or particles; we can talk of 1 mol of an element or a compound. Thus, mass of 1 mol of any substance will be its molar mass (*M*). Thus 1 mol of sodium means 6.022×10^{23} atoms of sodium weighing 23.0 g. In brief we can write

Molar mass of sodium, $M = 23.0$ g mol^{-1}

Similarly, 1 mol of oxygen molecule (O_2) means 6.022×10^{23} molecules weighing 32.0g or

Molar mass of oxygen (O_2), $M = 32.0$ g mol^{-1}

In case of NaCl if we say 1 mol of sodium chloride, we mean of 6.022×10^{23} formula units of NaCl, which will weigh 58.5g. Therefore, molar mass of NaCl = 58.5 g mol^{-1} (1 mol formula unit of NaCl will contain 1 mol of Na^+ and one mol of Cl^- ions).

In case of certain substances it is sometimes not very clear whether we are talking of 1 mol atom or 1 mol molecule. For example, if we say 1 mol of hydrogen, it means we are talking of naturally occurring form of hydrogen and it is

H_2 i.e. we are talking of 1 mol of hydrogen molecule. Sometime we specify very clearly, for example 1 mol atom of hydrogen. Here it is clear that we are talking of 1mol atom not molecule. But if it is not mentioned, then we should infer that it is the natural form of that substance. In order to avoid this confusion the molecular forms of nitrogen, hydrogen and oxygen are called dinitrogen (N_2), dihydrogen (H_2) and dioxygen (O_2).

Molar Volume of a substance is volume of one mole of that substance. Molar volume of liquid and solids can be calculated easily if we know the molar mass and density at any given temperature and pressure as these do not change much with temperature and pressure. The molar volumes for gases change considerably with temperature and pressure. For an ideal gas (which you will study in Unit - 2) molar volume at 0° C and 1 atm pressure (1.01bar) is 22.4L.

1.10.2 Mass-Mole Number Conversions

Molar masses can be thought of as conversion factors between masses in grams and number of moles. In order to determine the amount of an elemental sample, we can measure its mass and convert to mole by dividing by the molar mass of that element. Similarly; if we wish to know the *mass* of a particular *number of moles* of an element, we can multiply that number of moles by the elemental molar mass.

Suppose an ornament contains 16.8 g of silver, then it (ornament) contains

$$\frac{16.8\text{g}}{107.86\text{g mol}^{-1}} = 0.156\ \text{mol Ag}$$

Here we have divided mass of silver by its molar mass 107.86 g mol^{-1}. Similarly suppose we require 0.250 mol of Ag for a chemical reaction, it means we require (0.25 mol of Ag) × (107.86 g mol^{-1}) = 27.0 g silver.

If we wish to know how many silver atoms are present in the ornament (in the example cited above), we multiply 0.156 mol by Avogadro constant, 6.022×10^{23} atoms mol^{-1} (0.156 mol Ag) (6.022×10^{23} *atoms* mol^{-1}) = 9.39×10^{22} *atoms of Ag*. These relationships between mass, mole and number of entities of a substance are illustrated in Fig.1.3.

1.11 PERCENTAGE COMPOSITION AND MOLECULAR FORMULA

For the systematic study of a compound the first step is to determine its chemical formula. This can be achieved by analysing the compound for the amounts of the elements (moles) in a given mass of the compound. The results so obtained are expressed as the percentage composition – that is, *as the mass percentage of each element in the compound.*

According to *law of definite proportions* any sample of a pure compound always consists of the same elements combined in the same proportions by mass. Every molecule of ammonia always has the formula NH_3, i.e. 1 mol of ammonia always contains 1 mol of N and 3 mol of H. In other words, 17.0 g of NH_3 always contains 14.0 g of N and 3.0 g of H.

Mass % of N in NH_3

$$= \frac{\text{Mass of N in 1 mol of } NH_3}{\text{Mass of 1 mol of } NH_3} \times 100\%$$

$$= \frac{14.0\text{g N}}{17.0\text{g } NH_3} \times 100\% = 82.35\%$$

(or 82.35 g N per 100.0 g NH_3)

Mass % of H in NH_3

$$= \frac{\text{Mass of H in 1 mol of } NH_3}{\text{Mass of 1 mol of } NH_3}$$

$$= \frac{3.00\text{g H}}{17.0\text{g } NH_3} \times 100\% = 17.65\%$$

(or 17.65g H per 100.0 g NH_3)

Fig 1.3 Scheme for interconversion of mass, mole and number of entities

The molecular composition can be expressed in either of the following three equivalent ways:

(i) A formula giving the number of atoms of each type per molecule
(ii) Number of moles of each element per mole of a compound
(iii) Mass of each element per 100g of a compound (per cent composition)

1.11.1 Empirical and Molecular Formula

We have just seen that if the formula of a substance is known, we can determine its percentage composition. Conversely if we know the percentage composition of the elements by chemical analysis we can calculate the relative number of atoms of each element in the molecule of the compound. This gives us the empirical formula of the compound. Further if the molecular mass is known then the molecular formula can easily be determined. Thus, while *the* ***empirical formula*** *of a compound is a chemical formula showing the relative number of atoms in the simplest ratio, the* ***molecular formula*** *gives the actual number of atoms of each element in a molecule.* The molecular formula is generally an integral multiple of the empirical formula. In order to demonstrate how per cent composition data is used to find relative number of atoms of each type in a molecule, let us consider the example of hydrazine. A sample of hydrazine consists of 87.42% N and 12.58% H by mass. It means that a 100.0 g sample of hydrazine contains 87.42 g of N and 12.58g of H. Therefore, the number of moles of each element in the 100.0 g sample is

$$87.42\ \cancel{g\ N}\left(\frac{1\ mol\ N}{14.01\ \cancel{g\ N}}\right) = 6.24\ mol\ of\ N$$

$$12.58\ \cancel{g\ H}\left(\frac{1\ mol\ H}{1.00\ \cancel{g\ H}}\right) = 12.58\ mol\ of\ H$$

Let us now use the number of moles of each element in 100.0 g of sample to find out the number of moles of one element *relative* to the other. Thus, we have:

$$\frac{12.58\ mol\ of\ H}{6.24\ mol\ N} = \frac{2.00\ mol\ H}{1.00\ mol\ N}$$

showing that for hydrazine, the ratio is 2 mol of hydrogen to 1 mol of nitrogen. This means that in a molecule of hydrazine, the ratio of hydrogen to nitrogen is 2 : 1 and the empirical formula for hydrazine is NH_2. The molecular mass of hydrazine is 32.0 g mol^{-1} whereas the empirical formula mass for hydrazine is 16.0 g mol^{-1}, therefore, the molecular formula for hydrazine is $\frac{32}{16}$ times, the empirical formula, i.e. $NH_2 \times 2 = N_2H_4$.

The molecular formula conveys two important pieces of information

(1) The relative number of each type of atom in a molecule (the atom ratio)
(2) The total number of atoms of each element in the molecule.

Example 1.2

Naphthalene (moth balls) contains 93.71% carbon and 6.29 % hydrogen. If its molar mass is 128 g mol^{-1}, calculate its molecular formula.

Solution

From the data given it is clear that if we have 100.0 g of naphthalene, there are 93.71 g of C and 6.29 g of H. Number of moles of C and H in 100.0 g sample of naphthalene are

$$93.71\ g\ C\left(\frac{1\ mol C}{12.0 g C}\right) = 7.80\ mol C$$

$$6.29\ g\ H\left(\frac{1\ mol\ H}{1.00\ g H}\right) = 6.29\ mol\ H$$

$$\text{Mole ratio} = \left(\frac{7.80\ mol\ C}{6.29\ mol\ H}\right) = \left(\frac{1.24\ mol\ C}{1.00\ mol\ H}\right)$$

Changing the decimal fraction into whole number ratio of C and H, we know $1.24 \cong \frac{5}{4}$. Therefore, the ratio of C to H is

$$\text{Mole ratio} = \frac{5/4\ mol\ C}{1\ mol\ H} = \frac{5\ mol\ C}{4\ mol\ H}$$

The ratio of carbon to hydrogen atoms in naphthalene is 5 : 4, giving the empirical formula, C_5H_4. The ratio of molecular mass to

the empirical mass gives the factor with which the empirical formula is multiplied to obtain the molecular formula.

$$\frac{128\text{g / mol of napthalene}}{64.0\text{g / mol of } C_5H_4} = 2.00$$

Thus, molecular formula of naphthalene is given by empirical formula multiplied by 2, i.e. $(C_5H_4)_2$ or $C_{10}H_8$.

1.12 CHEMICAL STOICHIOMETRY

The method described for determining atomic and molecular masses constitute the beginning of a general approach to chemical calculations and quantitative methods called **Chemical Stoichiometry**.(Stoichiometry is derived from the Greek words *Stoicheion* = *element* and *metron* = *measure*). Stoichiometry is that area of chemistry and chemical technology on which the determination of the *quantities* of *reactants* (i.e. substances entering into chemical reaction), or *products* of a chemical reaction, is based. Here, the quantity of substances ranges from laboratory scale – generally grams and milligrams to plant production scale that could be few kilograms to several tons. In all such cases, we have seen that atoms and molecules combine in definite ratios in terms of number and in terms of their amounts. You have already learnt that a chemical reaction can be expressed in the form of a chemical equation from which we obtain a large amount of qualitative or quantitative information. Let us take a chemical reaction between nitrogen and hydrogen in the presence of a catalyst.

$$N_2(g) + 3H_2(g) \xrightarrow{\text{catalyst}} 2NH_3(g)$$

1 molecule of nitrogen + 3 molecules of hydrogen ⟶ 2 molecules of ammonia

Multiplying by 6.022×10^{23} the entire equation, we get,

$1\times6.022\times10^{23}$ molecules of nitrogen + $3\times6.022\times10^{23}$ molecules of hydrogen → $2\times6.023\times10^{23}$ molecules of ammonia

1 mol of nitrogen + 3 mol of hydrogen → 2 mol of ammonia

Taking molar mass into consideration

28.0 g of nitrogen + 6.0 g of hydrogen → 34.0 g of ammonia

Example 1.3

Hydrogen reacts with nitrogen to produce ammonia according to this equation:

$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$

Determine how much ammonia would be produced if 200.0 g of hydrogen react.

Solution

Let us first find out the amount (moles) of hydrogen involved.

$$\text{Amount (in moles) of } H_2 = \frac{\text{Mass of } H_2}{\text{Molar mass of } H_2}$$

$$= \frac{200.0\text{g of } H_2}{2.0\text{g mol}^{-1}} = 100.0 \text{ mol } H_2$$

According to the balanced chemical equation, amount of NH_3 produced (in moles) = 2/3 (mol of H_2 consumed)

= 2/3 (100.0 mol of H_2 consumed)

= 66.6 mol of NH_3

Mass of NH_3 produced

$$= (66.6 \text{ mol } \cancel{NH_3}) \left(\frac{17\text{g}}{\text{mol } \cancel{NH_3}} \right) = 1132.2 \text{ g}$$

Qualitatively a chemical equation simply describes what the reactants and products are. However, a **balanced chemical equation** gives a lot of quantitative information about a chemical reaction. It provides the ratio between the number of particles (atoms or molecules) of the reacting substances and number of particles (atoms or molecules) of the products formed. It also provides a quantitative relationship between masses of the reactants and products.

Quantity of a substance consumed or produced can be determined only if we use a balanced chemical equation. Therefore, it is relevant to know how to balance a chemical equation. You are already familiar with the balancing of a chemical equation and for your recapitulation it is again given here in the box. However, you will learn more about balancing of complex equations in Unit-9.

Balancing a chemical equation

According to the law of conservation of mass, a balanced chemical equation has the *same number of atoms of each element on both sides* of the equation. Many chemical equations can be balanced by *trial and error*. Let us take the reactions of a few metals and non-metals with oxygen to give oxides

$4\ Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$ (a) balanced equation

$2\ Mg(s) + O_2(g) \longrightarrow 2MgO(s)$ (b) balanced equation

$P_4(s) + O_2(g) \longrightarrow P_4O_{10}(s)$ (c) unbalanced equation

Equations (a) and (b) are balanced since there are same number of metal and oxygen atoms on each side of equations. However equation (c) is not balanced. In this equation, phosphorus atoms are balanced but not the oxygen atoms. To balance it, we must place the coefficient 5 on the left of oxygen on the left side of the equation to balance the oxygen atoms appearing on the right side of the equation.

$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$ balanced equation

Now let us take combustion of propane, C_3H_8. This equation can be balanced in steps.

Step 1 Write down the correct formulae of reactants and products. Here propane and oxygen are reactants, and carbon dioxide and water are products.

$C_3H_8(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$ unbalanced equation

Step 2 *Balance the number of C atoms:* Since 3 carbon atoms are in the reactant, therefore, three CO_2 molecules are required on the right side.

$C_3H_8(g) + O_2(g) \longrightarrow 3CO_2(g) + H_2O(l)$

Step 3 *Balance the number of H atoms* : on the left there are 8 hydrogen atoms in the reactants however, each molecule of water has two hydrogen atoms, so four molecules of water will be required for eight hydrogen atoms on the right side.

$C_3H_8(g) + O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

Step 4 *Balance the number of O atoms*: There are ten oxygen atoms on the right side ($3 \times 2 = 6$ in CO_2 and $4 \times 1 = 4$ in water). Therefore five O_2 molecules are needed to supply the required ten oxygen atoms.

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

Step 5 *Verify that the number of atoms of each element is balanced in the final equation.* The equation shows three carbon atoms, eight hydrogen atoms, and ten oxygen atoms on each side.

All equations that have correct formulae for all reactants and products can be balanced. Always remember that subscripts in formulae of reactants and products cannot be changed to balance an equation.

1.13 STOICHIOMETRY AND PROBLEM SOLVING

Solving of stoichiometric problems requires a firm grasp of the mole concept, balancing of chemical equations, and care in the consistent use of the units.

Example 1.4

Oxygen is prepared by catalytic decomposition of potassium chlorate ($KClO_3$). Decomposition of potassium chlorate gives potassium chloride (KCl) and oxygen (O_2). If 2.4 mol of oxygen is needed for an experiment, how many grams of potassium chlorate must be decomposed?

Solution

According to the statement given above we write chemical equation as

$$KClO_3\ (s) \longrightarrow KCl\ (s) + O_2\ (g)$$

Now, balancing the chemical equation by inspection we get

$$2KClO_3\ (s) \longrightarrow 2\ KCl + 3O_2\ (g)$$

From the above equation, we find that for obtaining 3 mol of oxygen, we require 2 mol of $KClO_3$.

For 2.4 mol of oxygen, we need,

$$2.4\ \cancel{\text{mol of oxygen}} \left(\frac{2\ \text{mol of}\ KClO_3}{3\ \cancel{\text{mol of oxygen}}}\right)$$

$= 1.6$ mol of $KClO_3$

Molar mass of $KClO_3$

= (39 g for potassium + 35.5 g for chlorine + 48.0 g for oxygen) = 122.5 g mol^{-1}

Therefore, mass of $KClO_3$ required

= 1.6 mol × 122.5 g mol^{-1} = 196.0 g

Limiting Reactant: We have just seen that reaction stoichiometry depends on the balanced chemical equation. In other words, reactants in a reaction should be present in the molar proportions given by the chemical equation. Often substances that react with each other are not present in exactly the proportions required by the balanced chemical equation or in stoichiometric ratios. For example, if 2 mol each of hydrogen and oxygen are mixed and a spark is passed through the mixture, water is formed according to the equation

$$2H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (l)$$

Here, 2 mol of hydrogen react with only 1 mol of oxygen, it is obvious 1 mol of oxygen remains unreacted. In such a case, hydrogen is said to be the **limiting reactant (or limiting reagent)** because its amount limits the amount of the product (water) formed. Thus, the ***limiting reactant*** *(or limiting reagent) is the reactant that is entirely consumed when a reaction goes to completion.* A reactant that is not completely consumed is often referred to as the ***excess reactant***. The following problem is an example of a reaction with a limiting reagent where the masses of the reactants are given rather than the number of moles.

Example 1.5

If 20.0 g $CaCO_3$ is treated with 20.0 g of HCl, how many grams of CO_2 can be generated according to the following equation

$$CaCO_3\ (s) + 2HCl\ (aq) \rightarrow CaCl_2\ (aq) + H_2O\ (l) + CO_2\ (g)$$

Solution

To solve this problem, you need only ask how much of each is needed to react with the other according to above chemical equation

Molar mass of $CaCO_3$ = 100 g mol^{-1}

Molar mass of HCl = 36.5 g mol^{-1}

Molar mass of CO_2 = 44.0 g mol^{-1}

Let us arbitrarily * choose $CaCO_3$ which will react with 20 g of HCl

Mass of $CaCO_3$ required = 20.0 g of HCl ×

$$\left(\frac{1\ \text{mol HCl}}{36.5\text{g HCl}}\right)\left(\frac{1\ \text{mol}\ CaCO_3}{2\ \text{mol HCl}}\right)\left(\frac{100\text{g}\ CaCO_3}{1\ \text{mol}\ CaCO_3}\right)$$

$= 27.4$ g of $CaCO_3$

It means 20.0 g of HCl will require 27.4 g of

* *More appropriate way for determining limiting reagent is to find out the amount of product formed using both the reactants. The reactant that gives the smaller amount of product is limiting reactant.*

$CaCO_3$. Since there is only 20.0 g of $CaCO_3$, therefore, $CaCO_3$ must be the limiting reactant and HCl is present in excess of the stoichiometric ratio established by the balanced chemical equation.

Now, if entire quantity of limiting reagent reacts, how much of CO_2 is formed ?

Mass of CO_2 formed from 20g $CaCO_3$

$$= 20.0\text{g } CaCO_3 \left(\frac{1 \text{ mol } CaCO_3}{100\text{g } CaCO_3}\right)\left(\frac{1 \text{ mol } CO_2}{1 \text{ mol } CaCO_3}\right)\times$$

$$\left(\frac{44.0\text{g } CO_2}{1 \text{ mol } CO_2}\right) = 8.80 \text{ g } CO_2$$

Similarly, calculations with a limiting reactant involving moles may be solved.

1.13.2 Stoichiometry of Reactions in Solutions

Since reactions in solutions are by far the most common, we turn now to chemical calculations involving solutions. The first question to consider is how to express the amount of a substance present in a given volume of a solution? There are a number of ways of doing this. For example, we can state the concentration of a solution in terms of grams of a solute in 100 g of solution (which is popularly known as mass percentage or w/w%). However, the most convenient method is to state the number of moles of solute in a given volume of a solution. The **molarity** *of a solute in solution is defined as the number of moles of the solute present in one litre of solution.*

$$\text{Molarity, M} = \left(\frac{\text{Moles of solute}}{\text{Litres of solution}}\right)$$

Thus, the unit of molarity is moles per litre (mol L^{-1}) or moles per cubic decimetre (mol dm^{-3}). The symbol M is used as an abbreviation for mol L^{-1}.

Before we undertake the problems on stoichiometry in solution, let us see how we can calculate the concentration of a solution.

Example 1.6

A solution is prepared by dissolving 18.25g of sodium hydroxide (NaOH) in distilled water to give 200 mL of solution. Calculate molarity of sodium hydroxide solution.

Solution

Molar mass of NaOH = 40.0 g mol^{-1}

$$\text{Moles of NaOH} = \frac{18.25\text{g}}{40.0\text{g mol}^{-1}} = 0.4562 \text{ mol}$$

Volume of solution = 200 mL = 0.20 L

$$\text{Molarity} = \frac{0.4562 \text{ mol}}{0.20\text{L}} = 2.281 \text{ mol L}^{-1} = 2.281 \text{ M}$$

If we take a given volume of a solution of known molarity we can calculate the amount of solute in the solution. Let us illustrate by taking the following example.

Example 1.7

How many moles and how many grams of sodium chloride (NaCl) are present in 250 mL of a 0.50 M NaCl solution?

Solution

A 0.50 M NaCl solution contains 0.50 mol of NaCl in 1 L or 1000 mL of solution. Therefore number of moles of NaCl in 250 mL of solution

$$= \frac{0.50 \text{ mol} \times 250 \text{ mL}}{1000 \text{ mL}} \text{ NaCl} = 0.125 \text{ mol NaCl}$$

Molar mass of NaCl = 58.5 g mol^{-1}

Mass of 0.125 mol NaCl = 58.5g mol^{-1} × 0.125 mol

= 7.315 g ≅ 7.32 g

Acids like hydrochloric acid, sulphuric acid, and nitric acid are available as aqueous solutions. The solutions required in the laboratory are prepared by diluting a definite amount of the concentrated acid with water to a definite volume. If the density of the acid is known it is easy to calculate the molarity of the diluted acid solution.

Example 1.8

Concentrated aqueous sulphuric acid is 98% H_2SO_4 by mass and has a density of 1.84 g mL^{-1}. What volume of the concentrated acid is required to make 5.0L of 0.50M H_2SO_4 solution?

Solution

1.0 L of 0.50 M H_2SO_4 contains 0.50 mol of H_2SO_4

Therefore, 5.0 L of 0.5 M H_2SO_4 would contain

$$0.50 \text{ mol} \times \frac{5 \text{ L}}{1 \text{ L}} = 2.50 \text{ mol of } H_2SO_4$$

Molar mass of H_2SO_4 = 98.0 g mol^{-1}

Mass of 2.5 mol H_2SO_4 = 2.5 mol × 98.0 g mol^{-1}

= 245.0 g H_2SO_4

However, concentrated sulphuric acid is 98% by mass. Therefore, the mass of concentrated sulphuric acid, which contains 245.0 g H_2SO_4

$$= \frac{245.0\text{g} \times 100}{98} = 250.0\text{g (concentrated sulphuric acid)}$$

The density of the concentrated sulphuric acid is 1.84 g mL^{-1}. Therefore, the volume in mL containing 250.0 g of the acid

$$= \frac{250.0\text{g}}{1.84\text{g mL}^{-1}} = 135.85 \text{ mL}$$

In order to get 5.0 L of 0.50 M H_2SO_4 solution, we should take 135.85 mL of concentrated acid and add it to water till the final volume is 5.0 L.

When aqueous solutions are mixed, chemical reactions may take place. The amount of the products can be determined if the volumes of the solutions of the reactants and their molarities are known. Let us take a few examples to illustrate it.

Example 1.9

500 mL of 0.250 M Na_2SO_4 solution is added to an aqueous solution of 15.00 g of $BaCl_2$ resulting in the formation of the white precipitate of insoluble $BaSO_4$. How many moles and how many grams of $BaSO_4$ are formed ?

Solution

The balanced equation for the reaction is

$BaCl_2$ (aq) + Na_2SO_4(aq) → $BaSO_4$ (s)+2NaCl (aq)

We can find the number of moles of the reactants.

Since 1 L(or 1000 mL) of 0.25 M Na_2SO_4

= 0.250 mol

Therefore, 500 mL of 0.25M Na_2SO_4 contains

$$0.250 \text{ mol} \times \left(\frac{500\text{mL}}{1000\text{mL}}\right) = 0.125 \text{ mol of } Na_2SO_4$$

Molar mass of $BaCl_2$ = 208.2 g

Therefore, number of moles of $BaCl_2$ in 15.0 g of $BaCl_2$

$$= \frac{15.0\text{g}}{208.2\text{g mol}^{-1}} = 0.072 \text{ mol } BaCl_2$$

The reaction equation shows that 0.072 mol $BaCl_2$ should react with 0.072 mol of Na_2SO_4 to yield 0.072 mol $BaSO_4$.

(The reaction mixture contains excess of Na_2SO_4 and $BaCl_2$ is thus the limiting reactant.) To calculate mass of $BaSO_4$ in grams, we note that

Molar mass of $BaSO_4$ = 233.4 g mol^{-1}

Therefore, mass of 0.072 mol $BaSO_4$

= (0.072 mol) (233.4 g mol^{-1})

= 16.80 g $BaSO_4$

Example 1.10

Reaction, $2Br^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$, is used for commercial preparation of bromine from its salts. Suppose we have 50.0 mL of a 0.060 M solution of NaBr. What volume of a 0.050 M solution of Cl_2 is needed to react completely with the Br^-?

Solution

First let us find out the chemical amount of Br^- present.

$$\text{Amount of } Br^- = 0.05 \text{ L solution} \times \left(\frac{0.060 \text{ mol NaBr}}{1\text{L solution}}\right)\left(\frac{1 \text{ mol } Br^-}{1 \text{ mol NaBr}}\right)$$

$$= 3.00 \times 10^{-3} \text{ mol } Br^-$$

Next we use the chemical conversion factor of one mole of Cl_2 per two moles of Br^- to find moles of Cl_2 reacting,

$$\text{Moles of } Cl_2 \text{ reacting} = 3.00 \times 10^{-3} \cancel{\text{mol Br}^-} \left(\frac{1 \text{ mol } Cl_2}{2 \cancel{\text{mol Br}^-}}\right)$$

$$= 1.50 \times 10^{-3} \text{ mol } Cl_2$$

Finally, we find the volume of aqueous chlorine needed

$$= 1.50 \times 10^{-3} \text{ mol } Cl_2 \times \left(\frac{1\text{L } Cl_2 \text{ solution}}{0.050 \text{ mol } Cl_2}\right)$$

$$= 3.00 \times 10^{-2} \text{ L } Cl_2 \text{ solution}$$

Suppose we want to know the Cl concentration after the reaction has been completed. Each mole of Br that reacts gives one mole of Cl in the products, the chemical amount that is produced is 3.00×10^{-3} mol. However, calculation of concentration of Cl must be done very carefully. The final volume of the solution is the total volume, approximately equal to the sum of the 50.0 mL originally present and the 30.0 mL added giving 80.0 mL = 0.080 L.

The final concentration of Cl^-

$$[Cl^-] = \left(\frac{3.00 \times 10^{-3} \text{ mol}}{0.080 \text{ L}} \right) = 0.0375 \text{ M}$$

SUMMARY

Measurement of various physical quantities is essential in order to make chemistry a *quantitative science*. Although there are many different systems of measurements but scientists mostly use the *metric system*. *International System of Units* (SI Units) uses a particular selection of metric units. This is a *coherent system* of units and *in any calculation when all physical quantities are expressed in SI units, result will also be obtained in SI units*. This system has seven SI base units from which all other units, called *derived units* can be obtained. SI prefixes are used to show a larger or smaller magnitudes of the physical quantities. Any measurement of physical quantities has a **numerical value, units** and **precision**. Precision is expressed by using significant figures. *Dimensional analysis* is a technique of calculation using physical quantities in which units are included and treated in the same way as numbers. Using **dimensional analysis**, one can obtain the *conversion factor* or *unit factor* needed to express a quantity in a new unit. *In unit factor the numerators and denominators are expressed in different units but represent the same or equivalent amounts. Multiplying by unit factor is equivalent to multiplying by unity.*

Chemistry is the science of atoms and molecules and the changes these undergo. On the basis of composition/constitution, matter is classified into homogeneous and heterogeneous mixtures. A mixture can be separated by physical processes into its constituents. *Compounds* can be resolved by chemical transformations into *elements*. *Laws of chemical combinations* led to the statement of **atomic theory** by Dalton. *Laws of combining volume* and Avogadro hypothesis can be used to predict molecular formulae. Atomic and molecular masses could be determined with precision after the development of *mass spectroscopy* in early 1900s. It also revealed that most of the elements are mixture of isotopes, which differ in masses but have same chemical properties. **Atomic mass** is thus an average of the masses of isotopes of that element, weighed by their fractional natural abundance. ***Molecular masses*** *of compounds are obtained by adding the atomic masses of the constituent elements.*

Avogadro constant, N_A provides a link between the macroscopic world of the chemical substances and microscopic world of atoms and molecules. Avogadro constant is defined as the number of atoms in exactly 0.012 kg of ^{12}C and is equal to 6.022×10^{23} atoms mol^{-1}. This chemical amount of ^{12}C is called one ***mole***. ***Empirical formula***, which gives the simplest ratio, and ***molecular formula***, which gives the actual number of atoms of each element in a compound, are important in chemistry. Empirical formulas are more meaningful in case of ionic solids and liquids. In such cases ***formula mass*** instead of molecular mass is used. If empirical formula is known, ***percentage composition*** (by mass) of the element in a compound can be determined (given a table of atomic masses) and vice versa. The percentage composition can also be calculated if molecular formula is known but reverse is not true. Calculation of formula using percentage composition always gives empirical or simplest formula of a particular substance. If reactants and products in a chemical reaction are known, a balanced chemical equation can be written for that reaction. *The relationship between the masses of chemical reactants and products in a balanced chemical equation is* ***stoichiometry*** *of the reaction.*

If a reaction involves two or more reactants, the reactant that is consumed first, limiting the amount of product(s) is called ***limiting reactant*** or ***limiting reagent***. Stoichiometry of reactions in solutions is of vital importance as most of the reactions in chemistry take place in solutions.

EXERCISES

1.1 In what way study of Chemistry will be helpful for the following :
(i) In identifying three chemical processes used in your daily life.
(ii) In solving politico-cum-social problems for which inputs are required.
(iii) Preparing a good engineer.
(iv) Planning of chemical industries in your district.

1.2 Express the following in SI base units using power of 10 notation
(example 2.54 mm = 2.54×10^{-3}m)
(a) 1.35 mm (b) 1 day (c) 6.45 mL (d) 48μg (e) 0.0426 in
(Please make use of unit conversion factors given at the end of this book)

1.3 For a precious stone, '*carat*' is used for specifying its mass. If 1 carat = 3.168 grains (a unit of mass) and 1gram = 15.4 grains, find the total mass in kilogram of the ring that contains a 0.500 carat diamond and 7.00 gram gold.

1.4 Using the unit conversion factors, express the given measurements in the designated units
(a) 25 L to m^3 (b) 25 g L^{-1} to mg dL^{-1} (c) 1.54 mm s^{-1} to pm μs^{-1}
(d) 2.66 g cm^{-3} to μg μm^{-3} (e) 4.2 L h^{-2} to mL s^{-2}

1.5 Express each of the following in SI units
(i) 93 million miles (this is the distance between Earth and Sun)
(ii) 5 feet 2 inches (the average height of an Indian female)
(iii) 100 miles per hour (the typical speed of Rajdhani Express)
(iv) 14 pounds per square inch (atmospheric pressure)
(v) 0.74 Å (the bond length of hydrogen molecule)
(vi) 46°C the peak summer temperature in Delhi
(vii) 150 pounds (the average weight of an Indian male).

1.6 "The star of India" sapphire weighs 563 carats. If one carat is equal to 200 mg, what is the weight of the gemstone in grams?

1.7 Vanadium metal is added to steel to impart strength. The density of vanadium is 5.96 g/cm^3. Express this in SI unit $\left(\frac{kg}{m^3}\right)$.

1.8 State the number of significant figures in each of the following numbers :
(i) 2.653×10^4 (ii) 0.003688 (iii) 653 (iv) 0.368 (v) 0.0300

1.9 (a) Convert the following in kilogram
(i) 0.91×10^{-27} g (mass of electron)
(ii) 1 fg (mass of human DNA molecule)
(iii) 500 Mg (mass of jumbo jet(loaded)
(iv) 3.34×10^{-24} g (mass of hydrogen molecule)
(b) Convert into metre
(i) 7 nm (diameter of small virus)
(ii) 40 Em (thickness of Milky Way galaxy)
(iii) 1.4 Gm (diameter of Sun)
(iv) 41 Pm (distance of nearest star)

1.10 (a) Classify the following as pure substances or mixtures
(b) Separate the pure substances into elements and compounds and divide the mixtures into homogeneous and heterogeneous categories :
(i) graphite (ii) milk (iii) air (iv) diamond (v) petrol (vi) tap water (vii) distilled water (viii) oxygen (ix) 22 carat gold (x) steel (xi) iron (xii) iodized table salt (xiii)wood (xiv) cloud.

1.11 Define the following
(i) Average atomic mass (ii) Mole (iii) Molar mass (iv) Unit factor (v) Molarity (vi) Precision and Accuracy.

1.12 (a) Express the following numbers to four significant figures

(i) 5.607892 (ii) 32.392800 (iii) 1.78986×10^3 (iv) 0.007837

(b) Express the result of the following calculations to the appropriate number of significant figures.

(i) $\frac{3.24 \times 0.08666}{5.006}$ (ii) 0.58 + 324.65 (iii) 1.78986×10^3 (iv) $943 \times 0.00345 + 101$

1.13 Calculate the number of moles in the following masses (a) 7.85 g of Fe (b) 65.5 µg of carbon (c) 4.68 mg of Si (d) 1.46 metric tons of Al (1 metric ton = 10^3kg) (e) 7.9 mg of Ca.

1.14 In the commercial manufacture of nitric acid, how many moles of NO_2 produce 7.33 mol HNO_3 in the reaction: $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$

1.15 Use the data given in the following table to calculate the molar mass of naturally occurring *argon:*

Isotope	Isotopic molar mass	Abundance
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063%
^{40}Ar	39.9624 g mol^{-1}	99.600%

1.16 (a) When 4.2 g of $NaHCO_3$ (sodium hydrogen carbonate) is added to a solution of CH_3COOH (acetic acid) weighing 10.0 g, it is observed that 2.2 g of CO_2 is released into atmosphere. The residue is found to weigh 12.0 g. Show that these observations are in agreement with the law of conservation of mass.

(b) If 6.3 g of $NaHCO_3$ are added to 15.0 g CH_3COOH solution, the residue is found to weigh 18.0 g. What is the mass of CO_2 released in the reaction?

1.17 Carbon and oxygen are known to form two compounds. The carbon content in one of these is 42.9% while in the other it is 27.3 %. Show that this data is in agreement with the law of multiple proportions.

1.18 Calculate the number of atoms in each of the following (i) 52 moles of Ar (ii) 52 u of He (iii) 52 g of He

1.19 Potassium bromide KBr contains 32.9% by mass potassium. If 6.40 g of bromine reacts with 3.60 g of potassium, calculate the number of moles of potassium which combine with bromine to form KBr.

1.20 Write the empirical formulas of the compounds having molecular formulas:
(i) C_6H_6 (ii) C_6H_{12} (iii) H_2O_2 (iv) H_2O (v) Na_2CO_3 (vi) B_2H_6 (vii) N_2O_4 (viii) HPO_3 (ix) H_3PO_4 (x) Fe_2O_3 (xi) C_2H_2

1.21 Chlorophyll, the green colouring matter of plants responsible for photosynthesis, contains 2.68% of magnesium by mass. Calculate the number of magnesium atoms in 2.00 g of chlorophyll.

1.22 (a) Butyric acid contains only C,H, and O. A 4.24 mg sample of butyric acid is completely burned. It gives 8.45 mg of carbon dioxide (CO_2) and 3.46 mg of water. What is the mass percentage of each element in butyric acid ?

(b) If the elemental composition of butyric acid is found to be 54.2% C, 9.2% H and 36.6% O, determine the empirical formula

(c) The molecular mass of butyric acid was determined by experiment to be 88 u. What is the molecular formula?

1.23 (a) A sample of NaOH weighing 0.38 g is dissolved in water and the solution is made to 50.0 mL in a volumetric flask. What is the molarity of the resulting solution ?

(b) How many moles of NaOH are contained in 27 mL of 0.15 M NaOH ?

1.24 A sample of $NaNO_3$ weighing 0.38g is placed in a 50.0 mL volumetric flask. The flask is then filled with water to the mark on the neck. What is the molarity of the solution?

1.25 In a reaction vessel 0.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.150 M NaOH solution should be added for this requirement.

1.26 Zinc and hydrochloric acid react according to the reaction :
$Zn(s) + 2\ HCl\ (aq) \rightarrow ZnCl_2\ (aq) + H_2\ (g)$
If 0.30 mol Zn is added to hydrochloric acid containing 0.52 mol HCl, how many moles of H_2 are produced?

1.27 Commercially available concentrated hydrochloric acid contains 38% HCl by mass.
(a) What is the molarity of this solution? The density is 1.19 g mL^{-1}
(b) What volume of concentrated HCl is required to make 1.00 L of 0.10 M HCl?

1.28 $Fe_2(SO_4)_3$ is empirical formula of a crystalline compound of iron. It is used in water and sewage treatment to aid in the removal of suspended impurities. Calculate the mass percentage of iron, sulphur and oxygen in this compound.

1.29 A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide , 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula (ii) molar mass of the gas, and (iii) molecular formula.

1.30 Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction, $CaCO_3\ (s) + 2\ HCl\ (aq) \rightarrow CaCl_2\ (aq) + CO_2(g) + H_2O(l)$
What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl?

1.31 Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction
$4\ HCl\ (aq) + MnO_2(s) \rightarrow 2H_2O\ (l) + MnCl_2(aq) + Cl_2\ (g)$
How many gram of HCl react with 5.0 g of manganese dioxide?

1.32 Calculate the volume of 1.00 mol L^{-1} aqueous sodium hydroxide that is neutralized by 200 mL of 2.00 mol L^{-1} aqueous hydrochloric acid and the mass of sodium chloride produced. (Neutralization reaction is $NaOH\ (aq) + HCl(aq) \rightarrow NaCl\ (aq) + H_2O\ (l)$)

UNIT 2

STATES OF MATTER

"Chance favours the prepared mind"
- Louis Pasteur

Objectives

After studying this Unit, you will be able to

- explain the existence of different states of matter in terms of intermolecular forces and thermal energy.
- describe the behaviour of gases according to gas laws: Boyle's law, Charles' law, Dalton's law of partial pressures and Graham's law of diffusion/effusion.
- carry out calculations based on gas laws.
- interpret gas laws in terms of kinetic molecular theory of gases.
- explain the behaviour of real gases.
- describe some properties of liquids.
- classify and describe solids in terms of intermolecular forces.

It is well known that matter exists in solid, liquid and gaseous states. Solids have a definite volume and shape; liquids also have a definite volume but no definite shape; gases have neither a definite volume nor a definite shape. We also know that all matter is made up of atoms and molecules. In this Unit we will study about the aggregation of the molecules to the different states of matter. We will also explain their characteristic properties and discuss the laws governing their behaviour.

2.1 INTERMOLECULAR FORCES VERSUS THERMAL ENERGY

The three states of matter are the result of a competition between molecular interaction energy, which keeps molecules together and thermal energy which moves them apart (Fig. 2.1). This competition determines whether a given substance under given conditions is a gas, a liquid or a solid.

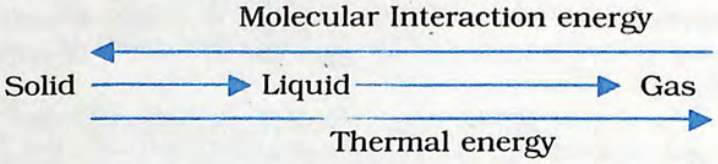


Fig. 2.1 *Change of state involves competition between ordering molecular interaction energy and disordering thermal energy*

Thermal energy is the energy possessed by matter by virtue of its temperature and is also a measure of thermal motion or movement of molecules. Molecular interactions lead to intermolecular attractive and repulsive forces. In gases, the molecules have almost no molecular interactions and their thermal motions are manifested as random translatory movements of molecules. In solids the molecular interactions are very strong. The molecules in solids have no translatory movement and only oscillate with respect to their equilibrium

position. In liquids the arrangement is in between these two extremes.

When the two molecules are far apart, they move independent of each other. At given pressure and temperature as the molecules come closer, the molecular interactions become important. The average speed of molecules in a gas increases with temperature and their motion become more random. In solids, the net forces between the molecules are attractive until as they get very close, the forces become repulsive. The molecules in a solid with relatively low thermal motion cannot break free of mutual attractions. However, on heating due to relative increase in thermal motion, the solid melts.

In the liquid state a fine balance exists between attractive intermolecular forces and thermal energy, so that the molecules can break away from one another and get attracted while approaching the other molecules. In solids and liquids intermolecular forces become repulsive when molecules are pushed together by external pressure. Therefore, the compressibility of liquids and solids is very small. The average intermolecular distance is not much different in a liquid or solid, hence, small changes in volume take place on their interconversion. Continuous breaking and making of bonds between molecules in liquid gives it a non-rigid structure. This explains why liquids do not have any definite shape although they have a definite attractive interaction energy between the molecules. In gases average distances between the molecules are large and hence the molecular interactions are weak. For gases like hydrogen and oxygen these may be neglected at high temperature and low pressure. The forces of repulsion come into play only during direct collision between the molecules. There are large empty spaces between the molecules and there is nothing to stop them from getting closer when pressure is applied. Hence the gases are highly compressible.

2.2 THE GASEOUS STATE

Pressure, volume, temperature, amount, viscosity, specific heat are some of the many measurable properties of gases. The amount, volume, pressure and temperature are most important properties as these four interdependent variables describe the state of any gas. The interdependence of these variables lead to formulation of different gas laws. Before we proceed to the gas laws let us learn a little about these four measurable variables.

(i) Amount, n

You have already studied in Unit 1 about amount of a substance and the relationship between mass and number of particles (atoms/molecules). The amount of the gas can easily be calculated, dividing its mass by its molar mass, $n = m/M$

(ii) Volume, V

The volume of a gas is the volume of the container in which the gas is confined. The volume is measured in litre or cubic metre and we know from Unit 1 that

$$1\ L = 10^{-3}\ m^3 = 1\ dm^3 = 10^3\ cm^3$$

(iii) Pressure, p

The force exerted by the gas per unit area on the walls of the container is equal to its pressure. In SI Unit, a force of 1 newton acting on a surface of 1 square metre exerts a pressure of 1 pascal, Pa, that is

$$1\ Pa = 1\ N\ m^{-2} = 1 kg\ m^{-1}\ s^{-2}$$

For gases this unit is too small and generally we express the pressure of gas in terms of bar and we have $1\ bar = 100\ kPa = 10^5\ Pa$

The older unit for measurement of pressure was atmosphere, atm, which is related to the SI Unit of pressure as given below :

$$1\ atm = 1.01325\ bar = 1.01325 \times 10^5\ Pa$$

or $\quad 1\ bar = 0.987\ atm$

You are already familiar from earlier classes that atmospheric pressure is measured by a device called barometer which consists of a long glass tube filled with mercury. Atmospheric pressure $p = hdg$; where 'h'is the height of the mercury column supported by the barometer, 'd' is the density of mercury and 'g' acceleration due to gravity. The pressure is obtained in pascal when h, d and g are expressed in SI unit.

A manometer is a device for measuring the pressure of a gas in a closed vessel. It is a simple device with a horizontal arm and a U tube carrying mercury or any other suitable liquid.

The vessel containing gas is connected to the horizontal arm of the manometer (Fig.2.2).

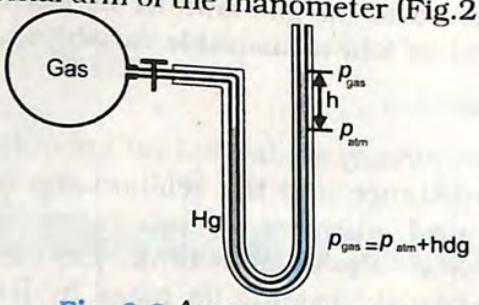


Fig. 2.2 An open arm manometer

(iv) Temperature, *T*

The temperature of a body is usually determined by using a Celsius thermometer and the SI unit of temperature is kelvin. The size of the degree on a kelvin scale is the same as on the celsius scale. The difference is only in terms of the location of zero. On the kelvin scale water freezes at 273.15K and boils at 373.15K at one atmospheric pressure.

2.3 GAS LAWS

We know that the volume of a gas depends on the amount, pressure and temperature. Gas laws are the simple quantitative relationships between any two of these variables when the other two are kept constant.

2.3.1 Boyle's law

Robert Boyle (1662), quantified the changes in volume of a gas by varying pressure at a constant temperature of a fixed amount of gas. He used a 'J' shaped (Fig. 2.3) glass tube. The gas under investigation can be trapped in this apparatus using mercury.

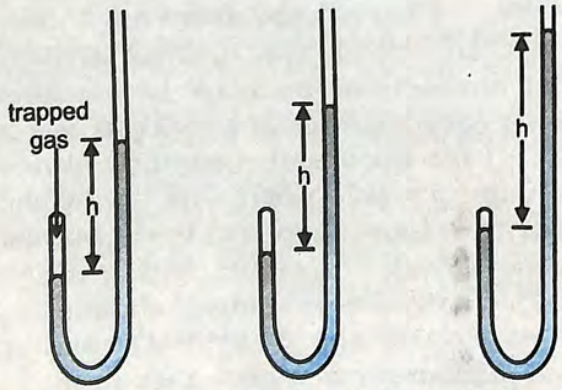


Fig.2.3 Boyle's apparatus for studying relationship between pressure and volume

Boyle's law states that the *pressure of a fixed amount of a gas varies inversely with the volume if the temperature is maintained constant.*

Mathematically the law is represented as

$p \propto 1/V$ (n, T constant) or

$V \propto 1/p$ (n, T constant)

i.e. p = constant/V

or pV = constant (n and T constant)

The value of constant depends upon n and T. At every temperature, therefore, for a fixed amount of gas there is a separate pressure–volume curve. A p-V curve at a constant temperature is called an isotherm. Shown below in Fig. 2.4 are three such isotherms.

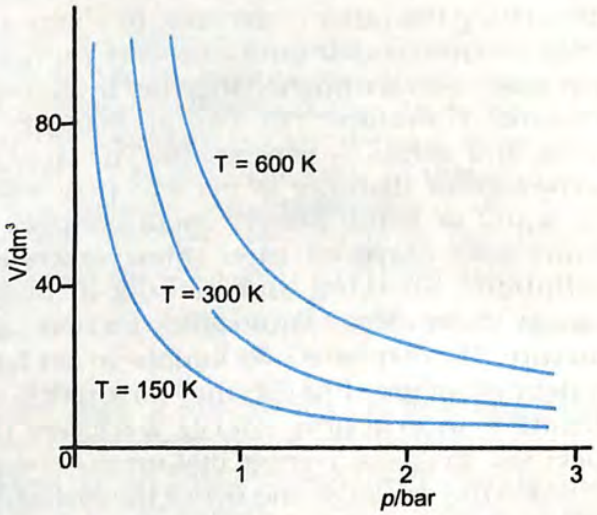


Fig. 2.4 Isotherms for a fixed amount of a gas

Table 2.1 gives variation in volume of 0.09mol carbon dioxide gas with pressure at 300K.

Table 2.1 Effect of Pressure on the Volume of 0.09 mol of CO_2 at 300K

Pressure/10^3Pa	Volume/10^{-3}m^3	(1/V) / m^{-3}	pV/10^2Pa.m^3
2.0	112.0	8.90	22.40
2.5	89.2	11.2	22.30
3.5	64.2	15.6	22.47
4.0	56.3	17.7	22.50
6.0	37.4	26.7	22.44
8.0	28.1	35.6	22.48
10.0	22.4	44.6	22.40

A plot of pV against p (Fig. 2.5) is a straight line parallel to the X-axis, showing that pV is constant at different pressures. A plot of $1/V$ against p (Fig. 2.6) is a straight line passing through the origin showing the pressure is inversely proportional to volume.

Thus, for a fixed amount of gas at a given temperature pV = constant and plot of p vs $1/V$, a straight line passing through the origin are two alternate ways of expressing Boyle's law.

Strictly speaking Boyle's law is obeyed only by a hypothetical gas called ***ideal gas***. However, gases like nitrogen, oxygen, carbon dioxide obey Boyle's law at low pressures and high temperatures, and behave as ideal gases.

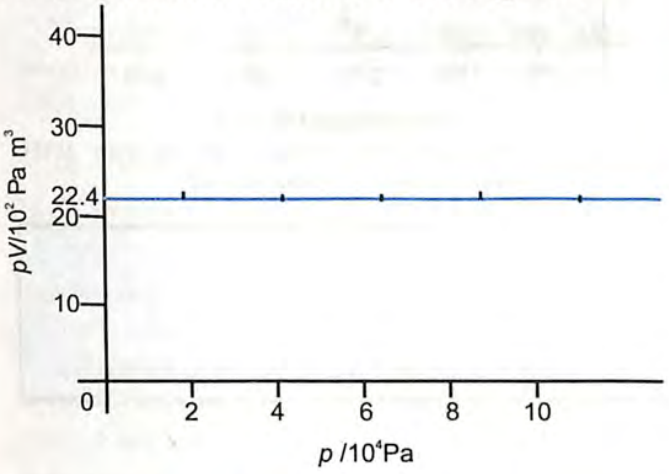


Fig. 2.5 *Plot of pV against p*

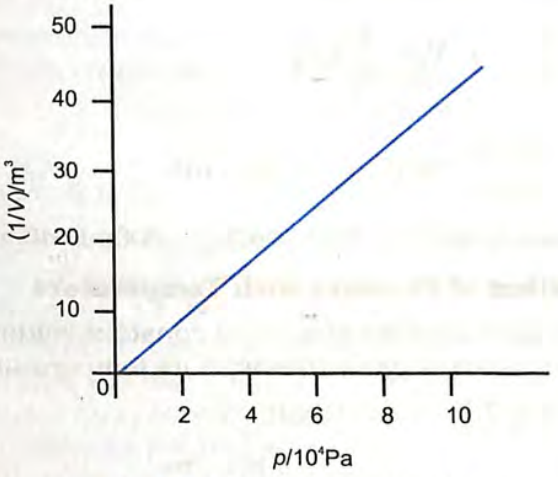


Fig.2.6 *Plot of 1/V against p*

A fixed amount of gas at a temperature T occupying a volume V_1 at pressure p_1, undergoes expansion so that the final volume becomes V_2 at pressure p_2. The initial and the final states can be related by Boyle's law as temperature and amount do not change.

$$p_1V_1 = p_2V_2$$

Knowing any three variables, the fourth can be computed.

Boyle's law can also be represented as

$$\frac{p_1}{p_2} = \frac{V_2}{V_1} \text{ (at } n, T \text{ constant).}$$

Any unit for pressure and volume can be used provided it is same for p_1 and p_2 ; V_1 and V_2.

Example 2.1

At a constant temperature, a gas occupies a volume of 200 mL at a pressure of 0.720 bar. It is subjected to an external pressure of 0.900 bar. What is the resulting volume of the gas?

Solution

Boyle's law is applicable as the amount and temperature are unaltered

$p_1 V_1 = p_2 V_2$

or $p_1 / p_2 = V_2 / V_1$ 'Substituting the values'

$0.720 \text{ bar} / 0.900 \text{ bar} = V_2 / 200 \text{ mL}$

$$V_2 = \frac{720}{900} \times 200 \text{ mL} = 160 \text{ mL}$$

Boyle's law is manifested in the working of many devices used in daily life such as cycle pump, aneroid barometer and tyre pressure gauge etc.

2.3.2 Charles' law

The French scientist, Jacques Charles in 1787 found that for a fixed amount of a gas at constant pressure, the gas expands as temperature increases.

Charles collected data at atmospheric pressure for different amounts of a gas and plotted the volume against temperature in °C. These plots when extrapolated intersect the temperature axis at the same point –273°C corresponding to zero volume. Similar results were obtained for other gases intersecting the temperature axis at –273°C (Fig.2.7). Charles concluded that all gases at this temperature could have zero volume and below this the volume would be negative. Charles knew that

zero and negative values of volumes are not possible physically. Therefore he thought that –273°C is the lowest possible temperature and called it, the absolute zero.

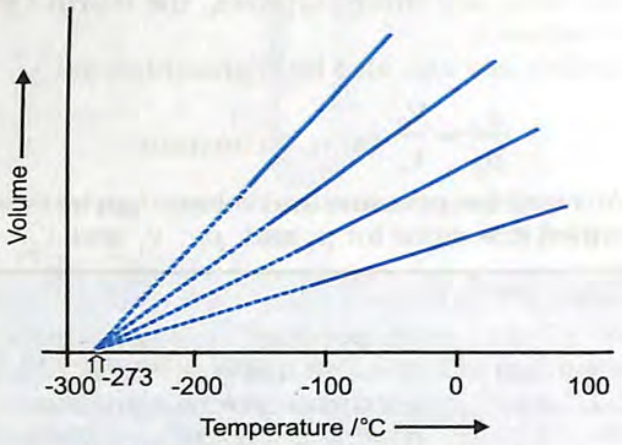


Fig.2.7 *Charles' law : Plot of V vs t°C*

Charles Law may be stated as : *pressure remaining constant, the volume of a fixed amount of a gas varies directly with its absolute temperature.* That is $V \propto T$ or V/T = constant [n,p constant]

Charles also found that for a given mass of a gas if pressure is kept constant the volume increases linearly with temperature.

$V = V_0 (1 + \alpha t)$ or $V - V_0 = V_0 \alpha t$

If the temperature is measured in the Celsius scale and V_0 is the volume at 0°C it is found that $\alpha = 1/273$ (Fig.2.8). The volume at temperature T is then

$$V_T = V_0\left(1+\frac{t}{273}\right) = V_0\left(\frac{273+t}{273}\right)$$

$$V_T = \frac{V_0}{273} T$$

where T=273 + t is the temperature on the kelvin scale, which has –273°C as its zero point.

To obtain temperature in absolute or kelvin scale, more precisely we add 273.15 to the temperature in the celsius scale. For simplification 273.15 is rounded off to 273, while dealing with pressure and volume, the temperature is always expressed in K in case of gases.

Charles' law may therefore also be stated as *the volume of a fixed mass of a gas at constant pressure increases or decreases by 1/273 of its volume at 0°C for 1° rise or fall in temperature.*

Like Boyle's law, Charles' law is also strictly obeyed by an ideal gas only but gases like nitrogen, oxygen and their mixtures obey Charles' law at very low pressures and high temperatures.

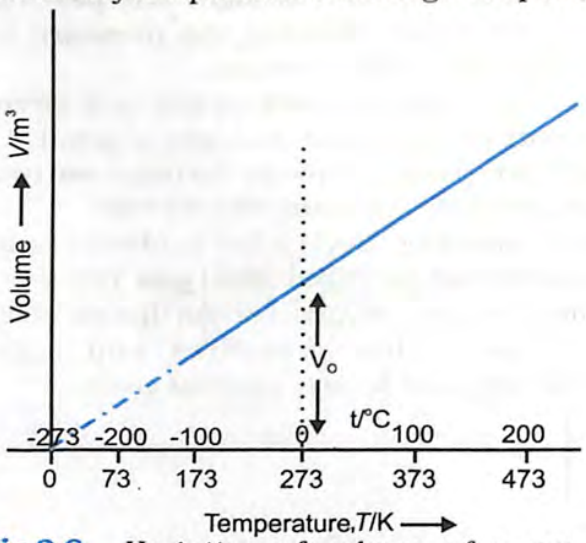


Fig.2.8 *Variation of volume of a gas with temperature (n, p constant)*

Example 2.2

What is the increase in volume, when the temperature of 600mL of air increases from 27°C to 47°C under constant pressure?

Solution

Charles law is applicable as the pressure and amount remains constant.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad V_1 = \frac{T_1}{T_2} \times V_2$$

$$V_1 = \frac{320\ K}{300\ K} \times 600\ mL = 640\ mL$$

Increase in volume of air =640mL - 600mL=40 mL

Variation of Pressure with Temperature

For a fixed amount of a gas at constant volume, the pressure of gas varies with its temperature.

$p \propto T$ (n, V constant)

$$\text{or } \frac{p}{T} = \text{constant} \quad \text{or} \quad \frac{p_1}{T_1} = \frac{p_2}{T_2}$$

2.3.3 Combined Gas Equation

The Boyle's and Charles' laws can be combined to give a relationship between the three variables p, V and T. Let a certain amount of a

gas in a vessel have a volume V_1, pressure p_1 and temperature T_1. On changing the temperature and pressure to T_2 and p_2 respectively, the gas occupies a volume V_2. This change can be carried out in two steps.

Step I : Keeping the temperature constant at T_1, the pressure changes to p_2 and the gas occupies a volume V.

Step II : Keeping the pressure constant at p_2 and the temperature is changed to T_2 the gas attains the final volume V_2.

The first step involves isothermal change. The process obeys Boyle's law therefore,

$p_1V_1 = p_2V$ (n, T_1 constant)

In the second step the pressure remains constant, the process obeys Charles' law Therefore, $V/T_1 = V_2/T_2$ (n, p_2 constant))

or $V = V_2 \times T_1/T_2$

Substituting for 'V' we obtain

$$p_1V_1 = \frac{p_2V_2T_1}{T_2} \quad \text{or} \quad \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

The above relation is called the *combined gas law.* Knowing any five variables the sixth can be calculated.

2.3.4 Avogadro law

The Avogadro law states that: *At a given temperature and pressure the volume of a gas is directly proportional to the amount of gas;* that is,

$V \propto n$ (p and T constant)

or V = constant × n

where 'n' is the amount of substance.

Amedeo Avogadro in the year 1811 generalized the above observation by the statement: *All gases containing equal amounts of substance occupy the same volume at the same temperature and pressure.* It is now known that 1mol of any gas at 0°C and under 1 bar pressure occupies 22.7×10^{-3} m^3 or 22.7 L.

It is further implied that molar volume V_m, for all gases at the same temperature and pressure has the same value. The total volume of the gas, V is equal to nV_m.

Avogadro further, generalized the statement that a mole of any substance contains 6.022×10^{23} particles (molecules, atoms or any other entities). This number is an important fundamental number, called Avogadro constant N_A. The relation between number of entities, number of moles and Avogadro's constant has already been discussed in Unit 1.

Example 2.3

Calculate the number of nitrogen molecules present in 2.8g of nitrogen gas.

Solution

Number of moles of nitrogen = 2.8g/28g mol^{-1} = 0.1mol

Number of nitrogen molecules

$= 0.1\,\text{mol} \times 6.022 \times 10^{23}\,\text{mol}^{-1} = 6.022 \times 10^{22}$

2.3.5 Ideal Gas Equation

As stated earlier, a hypothetical gas that would obey Boyle's and Charles' law under all conditions of temperature and pressure is called an ideal gas. Common gases like nitrogen, oxygen would show ideal gas behaviour at low pressures and high temperatures when the molecular interactions are negligible.

Here, we combine the four measurable variables, $p.V.T.$ and n; to give a single equation. Volume of a gas varies with n, T and p as given below:

$V \propto n$ [p, T constant] Avogadro's law

$V \propto T$ [n, p constant] Charles' law

$V \propto 1/p$ [n, T constant] Boyle's law

The combined gas law can be written as

$$V \propto \frac{nT}{p} \quad \text{or} \quad pV \propto nT \quad \text{or} \quad pV = nRT$$

where R is the constant of proportionality.

This equation is called **Ideal Gas Equation** and R is the molar gas constant.

From the equation we know that $R = pV/nT$. We also know that at a pressure of 1 bar and at temperature 273.15 K, the volume of 1 mol of a gas is 22.7 L = 22.7×10^{-3} m^3. Substituting these values in the above equation we find that

$$R = \frac{10^5\,\text{Pa} \times 22.7 \times 10^{-3}\,\text{m}^3}{1\,\text{mol} \times 273.15\,\text{K}} = \frac{10^5\,\text{Nm}^{-2} \times 22.7 \times 10^{-3}\,\text{m}^3}{1\,\text{mol} \times 273.15\,\text{K}}$$

$= 8.314\,\text{J mol}^{-1}\,\text{K}^{-1}$ (we know, Nm = J)

Example 2.4

If the density of a gas at the sea level at 0°C is 1.29 kg m^{-3}, what is its molar mass? (Assume that pressure is equal to 1 bar).

Solution

$pV_m = RT$ or $p.\ M/d = RT$ or $M = dRT/p$

$$= \frac{1.29 \text{kg m}^{-3} \times 8.314 \text{NmK}^{-1}\ \text{mol}^{-1} \times 273.15\text{K}}{1.0 \times 10^5 \text{Nm}^{-2} \text{(or Pa)}}$$

$$= \frac{1.29 \times 8.314 \times 273.15 \text{kg mol}^{-1}}{1 \times 10^5}$$

$= 0.0293 \text{kg mol}^{-1}$ or molar mass is 29.3 g mol^{-1}

2.3.6 Dalton's Law of Partial Pressures

So far we have been dealing with only pure gases. We shall now consider a mixture of non interacting gases. Let there be a mixture of two non-interacting gases say nitrogen and oxygen in a vessel. Both the gases would spread uniformly to occupy the volume of the vessel. The pressure of the mixture would then be the sum of the pressures exerted by the individual gases. *In a mixture the pressure exerted by the individual gas is known as its partial pressure.*

If p_{O_2} and p_{N_2} are the pressure of the individual gases respectively in their mixture, then pressure of the mixture, $p_{Total} = p_{O_2} + p_{N_2}$

Dalton's law of partial pressures can be stated as : *pressure exerted by a mixture of non-interacting gases is equal to the sum of their partial pressures.*

$p_{Total} = p_1 + p_2 + p_3 + \ldots$ (T and V constant)

where p_1, p_2, p_3 and so on are the partial pressures of the components 1,2 and 3 respectively. Air is a mixture of non-interacting gases and, therefore, the pressure exerted by air is the sum of the partial pressures of its components.

Example 2.5

A 2.5 L flask contains 0.25 mol each of sulphur dioxide, and nitrogen gas at 27°C. Calculate the partial pressure exerted by each gas and also the total pressure.

Solution

Partial pressure of sulphur dioxide,

$p_{SO_2} = nRT / V$

$$= \frac{0.25 \text{ mol} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 300\text{K}}{2.5 \times 10^{-3} \text{ m}^3}$$

$= 2.49 \times 10^5 \text{Nm}^{-2} = 2.49 \times 10^5 \text{Pa}$

Similarly $p_{N_2} = 2.49 \times 10^5 \text{Pa}$

Following Dalton's law

$p_{Total} = p_{N_2} + p_{SO_2}$

$= 2.49 \times 10^5 \text{Pa} + 2.49 \times 10^5 \text{Pa}$

$= 4.98 \times 10^5 \text{Pa}$

Partial Pressure in terms of mole-fraction

Mole fraction is a method of expressing concentration of a component in a mixture. Mole fraction, χ, defines the amount of a substance in a mixture as a fraction of total amount of all substances. If n_1 moles of any substance is present in n moles of the mixture, then mole fraction of the substance, $\chi_1 = n_1/n$.

If p_{N_2} is the partial pressure of nitrogen in the mixture of sulphur dioxide and nitrogen. Then

$p_{N_2} = n_{N_2}.RT/V$ (n_{N_2} is read as number of moles of nitrogen)

and $p_{mixture} = (n_{N_2} + n_{SO_2}).RT / V$

dividing we get

$p_{N_2} / p_{mixture} = n_{N_2} / (n_{N_2} + n_{SO_2}) = \chi_{N_2}$

or $p_{N_2} = \chi_{N_2} . p_{mixture}$

That is partial pressure of nitrogen in the mixture is the product of its mole fraction and total pressure of the mixture.

Application of Dalton's Law of Partial Pressures

The air pressure decreases with increase in altitude. This is why jet aeroplane flying at high altitude need pressurization of the cabins so that the partial pressure of oxygen is sufficient for normal breathing. It is for the same reason that mountaineers have to carry oxygen cylinders when climbing to higher ranges.

Many gases in the laboratory are collected by the downward displacement of water. A gas collected in this way also contains molecules of water that have evaporated into the gas. The

pressure exerted by these water molecules depends on the temperature of water. The partial pressure of water in the gas mixture collected is called the *aqueous tension* and is equal to the vapour pressure of water at that temperature. Table 2.2 gives the aqueous tension of water at different temperatures. The pressure of the dry gas is then obtained by subtracting aqueous tension from the observed pressure.

$P_{\text{dry gas}} = P_{\text{observed}}$ – aqueous tension

Table 2.2 Aqueous tension (vapour pressure) of water as a function of temperature

Temp./K	Pressure/bar	Temp./K	Pressure/bar
273.15	0.0060	295.15	0.0260
283.15	0.0121	297.15	0.0295
288.15	0.0168	299.15	0.0331
291.15	0.0204	301.15	0.0372
293.15	0.0230	303.15	0.0418

2.3.7 Graham's Law of Effusion/Diffusion

The ability of a gas to spread and occupy the whole available volume, irrespective of other gases present in the container is called diffusion. The aroma of the food that you smell near the kitchen is due to the diffusion of molecules with aroma through the air.

Effusion is the process by which a gas under pressure escapes from one chamber of a vessel through a small opening or an orifice. Escaping of air through a punctured tyre, escaping of perfume molecules through the atomizer are examples of effusion. The process of effusion is always followed by the process of diffusion.

Thomas Graham observed that lighter gases diffuse faster than the denser gases. In the year 1831, he proposed the law of effusion. The law states that **under identical conditions of temperature and pressure, the rate of effusion/ diffusion of a gas is inversely proportional to the square root of its density**, that is

rate of effusion $\propto \sqrt{1/d}$

or rate of effusion $= k\sqrt{1/d}$

where k is the constant of proportionality

or rate of effusion $\times \sqrt{d} = k$

If t_1, t_2 are the time required for the passage of the same volume, V_m, of two gases with densities d_1 and d_2 respectively at the same temperature and pressure, through the same orifice; then by definition,

rate of effusion = volume/time

$r_1 = V_m / t_1$

$r_2 = V_m / t_2$

dividing $r_1 / r_2 = t_2 / t_1 = \sqrt{(d_2 / d_1)}$

$= (d_2 V_m / d_1 V_m)^{1/2} = (M_2/M_1)^{½}$; $(d V_m = M)$

where M_1 and M_2 are the molar masses of two different gases

Example 2.6

Which of the two gases, ammonia and hydrogen chloride, will diffuse faster and by what factor?

Solution

$r_{NH_3} / r_{HCl} = (M_{HCl} / M_{NH_3})^{1/2}$

$= (36.5 / 17)^{1/2} = 1.46$ or $r_{NH_3} = 1.46 . r_{HCl}$

Thus ammonia will diffuse 1.46 times faster than hydrogen chloride gas.

The separation of isotopes, and other gaseous mixtures is based on this basic law. It also provides a method for the determination of molar mass.

2.4 KINETIC MOLECULAR MODEL OF A GAS

So far, we studied the macroscopic properties of gases and their relationships in the form of various gas laws. However, the gas laws do not explain the real nature of gases. For example, Charles' law tells us that for a given amount of gas volume is directly proportional to the absolute temperature, but it does not tell us why is it so ? In order to answer such questions, a theory based on a model is proposed. If the theoretical results on the basis of a particular model agree with the experimental observations, it indicates that the model is realistic.

The theory that provides an explanation for the various experimental observations about a gas is based on the Kinetic Molecular Model. It is assumed that all gases are made up of identical molecules, which are in a state of constant random motion.

2.4.1 Postulates of the Model

The kinetic molecular theory is based on the microscopic model of a gas. The predictions and calculations based on the model agree well with the experimental observations. This establishes the basic correctness of the model. The following are the postulates of this model:

i. **A gas consists of a large number of identical molecules of mass m. The dimensions of these molecules are very very small compared to the space between them.** Hence the molecules are treated as point masses.

ii. **There are practically no attractive forces between the molecules.** The molecules therefore, move independently.

iii. **The molecules are in a state of ceaseless and random motion, colliding with each other and with the walls of the container. The direction of their motions changes only on collision. These collisions are known as elastic collisions in which the energy and momenta of the molecules are conserved. In non-elastic collisions these quantities are not conserved.**

iv. **The pressure of a gas is the result of collisions of molecules with the walls of the container.**

v. **The average kinetic energy of the colliding molecules is directly proportional to its temperature.**

2.4.2 Distribution of Molecular Speeds

In a gas, we have a large number of molecules which constantly undergo collisions among themselves and with the walls of the container and there is exchange of energy, thereby changing their speed and kinetic energy. Therefore, at any instant different molecules in a gas have different speeds and hence different kinetic energies. We have molecules ranging from very small to very high speed. Even though the speed of individual molecule is constantly changing at a given temperature, the fraction of the molecules with a particular speed remains constant. This is known as distribution of speeds. This is also known as **Maxwell-Boltzmann Distribution law** as they were the first to formulate it. The maximum in distribution curve corresponds to the speed possessed by the highest fraction of molecules and is called the most probable speed, u_{mp}.

Fig.2.9 gives the distribution of speed of chlorine and nitrogen at a particular temperature. The maximum in each curve represents the most probable speed of the two gases respectively. The speed of a gas molecule at a given temperature also depends upon its mass. Lighter nitrogen molecules move faster than the heavier chlorine molecules. Hence nitrogen molecules have higher value of most probable speed than chlorine molecules at any given temperature.

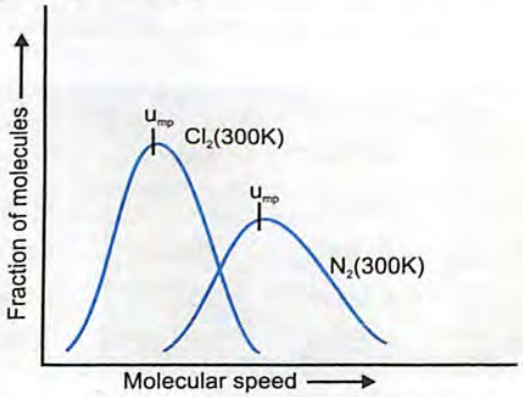


Fig.2.9 *Distribution of molecular speeds for chlorine and nitrogen at 300K*

The temperature dependence of distribution of speed for carbon dioxide at three different temperatures is shown in Fig.2.10. It is obvious from the distribution curves that the fractions of molecules with higher speed increases with increase in temperature. The value of most probable speed also increases at higher temperature. Besides the most probable speed, we also define the average and the root mean square speed. The average speed, u_{av}, as the name implies, is the mean of the speed of all the molecules i.e.

$$u_{av} = \frac{u_1 + u_2 + u_3 + \ldots + u_n}{n}$$

The mean square speed $\overline{u^2}$ is defined by

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \ldots + u_n^2}{n}$$

and the root mean square speed $u_{rms} = \sqrt{u^2}$ is the square root of the mean square speed of the molecules. The mean square speed is a direct measure of the average kinetic energy of a gas molecule. The three speeds are related by the

following relationships :

$u_{rms} > u_{av} > u_{mp}$

$u_{mp} : u_{av} : u_{rms} :: 1 : 1.128 : 1.224$

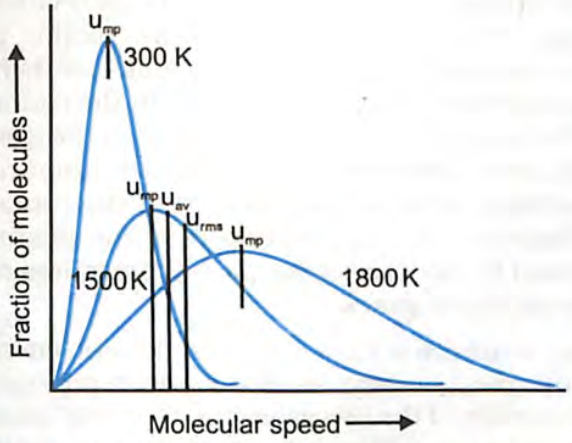


Fig.2.10 *Distribution of molecular speeds for carbon dioxide at different temperature*

2.4.3 Average Kinetic Energy of Molecules

The pressure of a gas in terms of this model as derived in box 2.1. is given below :

$$p = \frac{1}{3}(N/V)\, m\, \overline{u^2}$$

Using the above relationship and gas laws a connection between the average translational kinetic energy, $\frac{1}{2}m\overline{u^2}$, of a molecule at the temperature, T of the gas can be derived. Thus we have

$pV = RT$ [for one mole gas]

or $\frac{1}{3}N_A m\overline{u^2} = RT$

[$N = N_A$ for one mole of gas = Avogadro constant]

or $\frac{1}{2}m\overline{u^2} = \frac{3}{2}RT/N_A$

$= 3/2 \,.\, kT$ [$k = R/N_A$ = Boltzmann constant]

that is average transnational kinetic energy, $3/2kT$, of a molecule is directly proportional to the temperature of the gas. Also the average kinetic energy per mole of the gas is equal to $\frac{3}{2}RT$.

Box 2.1 : Pressure of an Ideal Gas

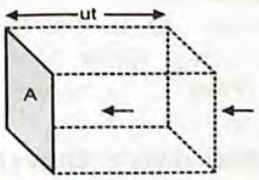


Fig.2.x *Imaginary box of length ut*

Assuming that molecules in a gas are travelling with a speed of u. A molecule which is within the imaginary box of length ut can only hit the wall A. Let us assume that a molecule with mass m travelling with a speed u strikes the wall with area A at right angles with a momentum mu. An equal and opposite momentum can stop the molecule. But the molecule bounces back from the wall with the momentum mu in opposite direction. Assuming the impact to be elastic that is there is no energy or momentum loss. The rate of change of momentum equals $-2mu$. In any elastic collision momentum must be conserved. *That is change of momentum of wall + change of momentum of the molecules = zero.* Therefore, the change of momentum of the wall is $2mu$. A molecule imparts a momentum $2mu$ to the wall. This change of momentum $2mu$ has taken place in time t.

Force = rate of change of momentum
Force acting on the wall = $2mu/t$

A molecule traveling with a speed u will travel distance ut in time t. Any molecule that is farther away than distance ut will not hit the wall. However all molecules within this imaginary space, Aut, will hit the wall. If N/V is the number of molecules per unit volume, then (N/V) Aut is the total number of molecules in the space that would hit the wall. Force acting on the wall is due to the force of impact of this number of molecules.

$$\text{Force on the wall} = \frac{2mu}{t} \times \frac{N}{V}.A\,u\,t$$

$$= 2(N/V)\, mu^2A$$

Now if we look at the diagram of the imaginary surface there will be 6 such walls where the molecules can strike. On an average one-sixth of the total number of molecules will hit one wall. That is, the force would be one-

sixth of that computed above or

$$\therefore \text{force} = \frac{2Nmu^2A}{6V} = \frac{1}{3V}Nmu^2A$$

$$\text{pressure} = p = F / A = \frac{1}{3V}Nmu^2$$

Now as the molecules don't travel with the same speed, the change in momentum and pressure they exert should all be averaged. An average is shown by writing a bar above u^2, like $\overline{u^2}$. The final equation for pressure of an ideal gas

$p = \frac{1}{3}\frac{N}{V}m\overline{u^2}$ where $\overline{u^2}$ is the square of the root mean square speed.

2.4.4 Explanation of Gas Laws on the Basis of the Kinetic Molecular Model

Let us see how the kinetic molecular model explains the different gas laws.

(i) Boyle's Law : The kinetic molecular model assumes that pressure of a gas is due to the collision of gas molecules with the walls of the container. The more the frequency of collisions, the higher would be the pressure. The reduction in the volume of the gas, increases the value of N/V to which pressure is directly proportional in the above model. Therefore as the volume of the gas is reduced the pressure increases, or in other words, the pressure is inversely proportional to the volume.

We have already derived that

$$1/2\, m\overline{u^2} = \frac{3}{2}kT \text{ also}$$

$$p = \frac{1}{3}(N/V)\, m\overline{u^2} \text{ or } p = \frac{2}{3}(N/V)\frac{1}{2}m\overline{u^2}$$

$$= \frac{2}{3}(N/V)(3/2)\, kT \text{ or } pV = N\,k\,T \text{ or } p \propto 1/V$$

From this equation it can be seen that at a constant temperature for a fixed number of gas molecules (equivalent to fixed amount $n=N/N_A$) the pressure is inversely proportional to volume.

(ii) Charles' Law : From the above relation $pV = N\,k\,T$, it can be seen that at constant pressure and for constant amount of gas ($n=N/N_A$), volume is directly proportional to the temperature which is the statement of the Charles' Law.

(iii) Dalton's Law : It is assumed that there are no attractive forces between the molecules of a gas. This is true when non-interacting gases are present together. Each molecule behaves independently of all the others in the container. The pressure of each component in the gaseous mixture depends only upon its amount, or number of molecules present in the container. Therefore, the total pressure of the mixture is equal to the sum of the partial pressures of the constituent gases.

(iv) Graham's Law : Average kinetic energy of any gas is same at the same temperature. Therefore of the two gases the one with the lower molar mass will have higher speed, hence it will effuse/diffuse faster.

2.5 REAL GASES

Nitrogen, oxygen, carbon dioxide are the commonly known gases. These gases are called real gases. It is observed experimentally that the gas laws, such as Boyle's law, Charles' law are obeyed by real gases only at low pressures and high temperatures. It may also be noted that all real gases start showing deviations from these laws at higher pressures and lower temperatures. All gases condense at higher pressures and sufficiently low temperatures.

It is difficult to determine quantitatively the deviation of a real gas from ideal gas behaviour from the pressure – volume curve as shown in Fig. 2.11. Compressibility factor Z defined by the equation.

$$pV = Z\, n\, RT$$

or $Z = pV / nRT = pV_m/RT$

is more suitable for a quantitative description of the deviation from ideal gas behaviour.

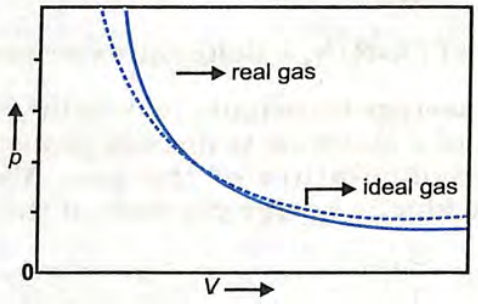


Fig.2.11 *Plot of pressure against volume for ideal and real gases*

Fig.2.12 gives compressibility factor at different pressures for some common gases. For ideal behaviour the compressibility factor is equal to one under all conditions of pressure and temperature. Value of Z different from one indicates non-ideal behaviour. Note that at pressure approaching zero that is at a very low pressure, the curves for different gases approach Z = 1, although with different slopes.

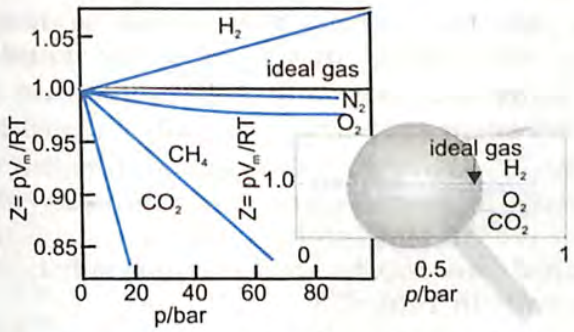


Fig. 2.12 Z as a function of p at 273K

A plot of Z against *p* for some common gases, in Fig. 2.13 shows some variations. Z values if less than one (Z<1) as for CH_4, CO_2, can be attributed to the predominance of attractive forces among the molecules of these gases at the temperature of experimentation whereas Z values if greater than one (Z >1) can be attributed to the dominance of strong repulsive forces among the molecules. All gases at sufficiently high pressure, when size of molecules are comparable to the volume of the gas, will have Z >1 when repulsive forces are dominant.

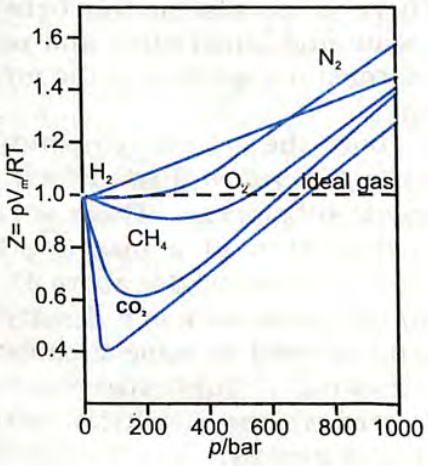


Fig. 2.13 Variation of compressibility factor for some gases at 273 K

2.5.1 Explanation for Deviation from Ideal Gas Behaviour

The deviation of real gases from the ideal gas behaviour is mainly due to two assumptions made while formulating the kinetic molecular theory :

i. The molecules were considered as point masses. However all real molecules have definite volume which cannot be neglected when the volume occupied by the gas is small.

ii. It was assumed that there are no intermolecular forces and molecules moved independently. This too is not true as otherwise gases would not condense into liquid.

Considering that the molecules of a gas are hard spheres of radius 2.0×10^{-10} m, the volume of the molecuies to the volume of the gas at room temperature and 1 bar pressure is about 0.1%, and about 1% at 10 bar. Thus the space available to the gas molecules for free movement decreases as the pressure increases.

With increase in pressure the average distance between molecules decreases when molecular interactions start operating. The number of molecular collisions with the walls of the container gets affected resulting in smaller values of pressure than what actually would have been in the absence of intermolecular interaction. It has been found that actual pressure exerted by oxygen gas at 1 bar and 0°C would have been 1.003 bar had it behaved ideally.

At very low pressures when the volume of a gas is very large; the volume of the gas molecules can be neglected. Under this condition the molecules on an average are far apart and at such distances molecular interactions are negligible.

2.5.2 Equation of State of Real Gas

Based on the above arguments, van der Waals suggested a modified gas equation, which describes the behaviour of real gases over wider range of pressure and temperature. The van der Waals equation for one mole of gas is written as :

$$(p + \frac{a}{V^2})(V - b) = RT$$

If *n* mole of gas are present in volume *V*; the

volume of one mole of gas would be $\frac{V}{n}$. So van der Waals equation has the form

$$\left(p + a/\left(\frac{V}{n}\right)^2\right)\left(\frac{V}{n} - b\right) = RT$$

$$\text{or } \left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

where p, V and T are the observed pressure, volume and temperature for the gas under study. 'a' and 'b' are the van der Waal's parameters which vary from gas to gas. The parameters a and b take care of the intermolecular forces and the size of the molecules respectively.

2.6 LIQUEFACTION OF GASES AND CRITICAL POINT

As mentioned earlier all gases can be condensed into liquids at sufficiently low temperatures, however, carbon dioxide condenses even at room temperature under high pressure. Thomas Andrew noted that carbon dioxide liquefied below 31.1°C by increasing pressure. It could not be liquefied above 31.1°C inspite of high pressure. This led him to call 31.1°C as critical temperature, T_c, for carbon dioxide. Fig.2.14 shows the isotherms of carbon dioxide gas obtained by plotting Andrew's data. The minimum pressure necessary to liquefy any gas at its critical temperature is called the critical pressure, p_c, and the corresponding volume occupied by one mole of the gas is called critical volume, V_c.

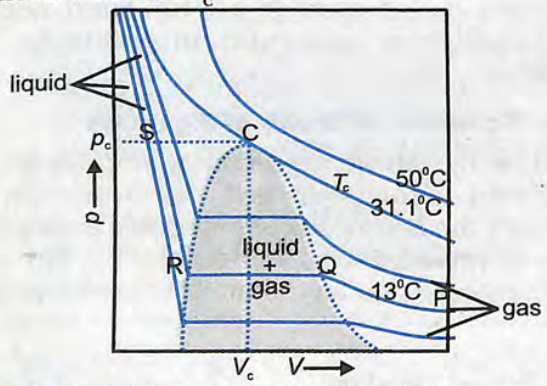


Fig.2.14 Isotherms of CO_2 and critical temperature

At 50°C the isotherm for carbon dioxide looks similar to that for ideal gas. As the temperature is lowered the deviation from the expected theoretical curve becomes more and more pronounced. At a low temperature say 13°C the isotherm PQRS consists of three parts. The volume of the gas decreases along PQ as the pressure increases. Along the horizontal portion QR there is considerable change in volume with no change in pressure, indicating process of liquefaction. At R when the liquefaction is complete the isotherm rises steeply as there is very little change in volume of the liquid as pressure increases. At 31.1°C the isotherm has a very small flat portion, virtually reduced to a point, C. Above 31.1°C under all pressures it remains in gaseous state. *Generally gases below their critical temperatures are called vapours.* Critical constants for some common substances are given in Table 2.3.

Table 2.3 Critical Constants for Some Substances

Substance	T_c /K	p_c /bar	V_c/dm^3 mol^{-1}
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126.	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.10	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

At the critical point the densities of a substance in gaseous and liquid states are same. There is no distinction between the gaseous state and liquid state and no second phase is formed irrespective of the pressure of the system.

Fluids above the critical temperatures are known as *super critical fluids* which dissolve many organic substances. These are used for speedy separation of a mixture into its components. Carbon dioxide above 31.1°C and above 600 bar pressure has a density around 1g/cm^3 and is used to remove caffeine from coffee beans, instead of using chlorofluorocarbons, which are not environmental friendly.

2.7 THE LIQUID STATE

We all know that on cooling steam changes into

liquid water and on further cooling it is converted into ice. The liquid state is intermediate between gaseous and solid states. We have already noted that in the gaseous state the molecular interactions are very weak practically negligible and molecules are in random motion. Molecules continue to move unless they are reflected back by the walls of the vessel. Otherwise molecules would continue to move and the gas would expand to any volume. This is why gases do not have a definite volume.

In case of liquid, the molecular interactions are quite strong and a given quantity of liquid, like solid(and unlike gas) occupies a definite volume. On the other hand the molecules of the liquid have so much freedom (unlike the molecules of a solid) that they can flow (translate) readily and take up the shape of the container due to continuous breaking and making of weak van der Waals bonds between the neighbouring molecules. In the liquid state neither random motion observed in gas nor the order of the solids (Section 2.8) is present .

Molecules in solids completely lack in translation motion. The molecular interaction energy practically over powers the thermal energy. The thermal motion of the molecules are so greatly reduced that they can only oscillate with respect to their fixed positions in the crystals. Each molecule in a solid has generally 6 to 12 nearest neighbours called coordination number. In the liquid state the coordination number of a molecule is not fixed but is only slightly less than in solid. The distance between the nearest neighbours in liquid is only slightly higher than that in solids. This is why there is very little expansion of solids on melting.

Vapour pressure, surface tension and viscosity are some of the typical physical properties of liquids that arise because of the two competing forces – the molecular interaction and thermal energy.

2.7.1 Vapour Pressure

We have seen that one of the most important and useful concepts that evolves from the kinetic theory is the idea that there is distribution of kinetic energies and hence the molecular speeds, depending on the absolute temperature. Therefore, in any gas, liquid or solid at room temperature, a small fraction of molecules have relatively high kinetic energy Fig. 2.15. Some of these high energy molecules at the liquid surface become free resulting into its evaporation. With the departure of high energy molecules the average kinetic energy decreases leading to a fall of temperature of the liquid. This explains why evaporation causes cooling.

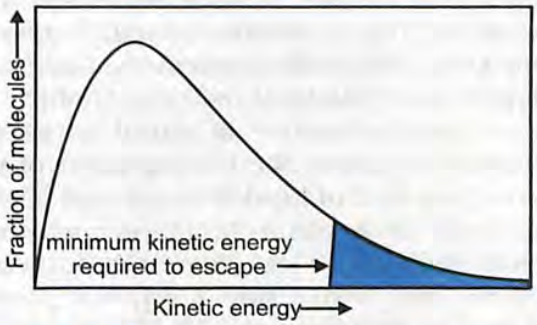


Fig.2.15 *Distribution of kinetic energy*

In an open vessel the liquid keeps on evaporating, as the liquid absorbs energy from the surroundings to replenish the energy loss due to evaporation. This increases the average kinetic energy and the process of evaporation continues till the liquid disappears.

In a closed vessel, with some free space above the liquid, the evaporated molecules cannot escape to the atmosphere. Initially the vapour pressure increases and then comes to a constant value. The volume of the liquid decreases initially and then becomes constant over a period of time. The molecules with higher kinetic energy leave the liquid surface and enter the vapour state where they are enclosed by the walls of the vessel. The loss of liquid molecules is accompanied by a small decrease in the volume of the liquid. In the meantime the space above the liquid is more and more occupied by the molecules and hence the pressure increases. The random motion results into redistribution of the kinetic energy of the molecules in the vapour state. Increase in pressure means more number of collisions with the walls of the container. One of the boundary walls for the vapours being the surface of the liquid, molecules which have lower kinetic energy condense at the surface of the liquid on collision with it. In the mean time the redistribution of the kinetic energy among the molecules of the liquid state, results into a fraction of molecules with higher kinetic energy. Thus there will be a condensation of molecules

from the vapour state to the liquid state and evaporation from the liquid state to the vapour state. Inside a closed vessel, the liquid and its vapours are in *dynamic equilibrium*. The pressure exerted by the vapour is then known as *equilibrium vapour pressure*. Since the vapour pressure is a kinetic phenomena, it is independent of the amount of a liquid. It only depends on the temperature. The temperature must, therefore, be specified with the vapour pressure of a liquid.

A liquid is said to be at its boiling temperature if its vapour pressure is equal to external pressure. Therefore, the boiling point of water in particular and of liquids in general decrease as altitude of a place increases where the external pressure is less than one atmosphere pressure. The water has a vapour pressure equal to 1 atmosphere at 373.15K which is the normal boiling point of water. Water will boil at lower temperature if the external pressure is less than one atmosphere. It is, therefore, difficult to soften food at hills. The pressure cooker that is used in houses, or the autoclaves used in hospitals to sterilize the surgical equipment increase the boiling point of water by increasing the pressure above one atmospheric pressure by using a weight covering the vent.

2.7.2 Vapour Pressure of Solids

Like liquids, solids also evaporate and hence exhibit a vapour pressure. The molecules of a crystalline solid vibrate with respect to their equilibrium position and are constantly colliding with the nearest neighbours. The collision results into distribution of kinetic energies. A small fraction of molecules at the surface of the solid possesses large enough kinetic energy to break away from the surface. The free molecules enter the vapour state. This process, whereby a solid is directly converted to its vapour state is called *sublimation*. Substances like ammonium chloride, iodine, camphor, solid carbondioxide sublime at ordinary temperature and pressure. Snow sublimes when the surrounding temperature is below 0°C. The white cloud like trail that we see coming out of the high flying jet is water vapours issuing from the exhausts of high flying jets, getting converted directly into microcrystalline ice which is slowly reconverted into water vapour without passing through the liquid state.

This property of sublimation is used in the process called **freeze drying**. Substances containing water are cooled below –10°C, at one atmospheric pressure. All the water molecules present freeze to ice. The system is then subjected to evacuation when water sublimes out leaving behind the non-volatile components. Instant coffee, tea, powdered milk, and many medicines that we take are all prepared by this method.

2.7.3 Surface Tension

Surface tension is one of the characteristic properties of liquids. Consider a liquid in equilibrium with its vapours, each molecule in the liquid state is influenced by the nearest neighbour molecules. A molecule in the bulk of liquid experiences equal attractive forces from all sides. There is no resultant force on the molecule which tries to move it in any direction. Whereas for a molecule at the surface of the liquid, the net attraction towards the liquid is greater than that towards the vapour state. This is represented in Fig.2.16. If the surface area of the liquid is increased, then molecules from the body of liquid state have to be brought to surface of the liquid requiring work to increase the surface area.

The energy required to increase the surface area of the liquid by one unit, is defined as its surface tension. It is represented by the Greek letter γ (gamma). The liquid surface, in the absence of any other force tends to attain a minimum area. The surface layer, therefore, behaves as a stretched membrane which tends to contract. Mathematically it can be shown that for a given volume, the sphere has the minimum area. When a mercury thermometer bulb breaks, mercury spreads in small spherical globules. The water drop in vacuum

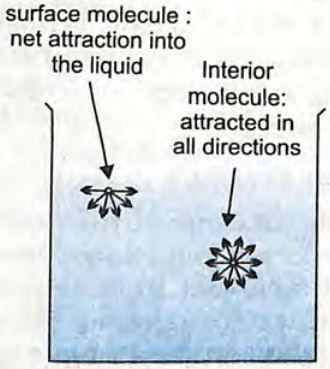


Fig.2.16 *Forces acting on a molecule on liquid surface and on a molecule inside the liquid*

is perfectly spherical. The shape of the water drop is distorted due to the action of gravity. Liquid in a capillary tube rises due to its surface tension, and this is one of the methods for the measurement of surface tension.

Surface tension is also defined as the force acting per unit length perpendicular to the line drawn on the surface. It has the dimensions of kg s^{-2} and its unit is expressed as N m^{-1} in the SI unit. It can also be expressed in terms of surface energy per unit area, as J m^{-2}.

2.7.4 Viscosity of Liquids

The ease with which a fluid can flow is determined by its property called *viscosity*. Viscosity arises due to the internal friction between layers of fluids as they pass over each other. When a liquid is steadily flowing over a fixed horizontal surface the layer immediately in contact with the surface is stationary. The velocity of the layers increases with the distance from the fixed surface. If we select a layer, the layer immediately below tries to retard its flow (velocity), while the one above tries to accelerate the flow. Force required to maintain the flow in the three layers described above is directly proportional to the area of contact and velocity gradient (Fig. 2.17).

Force is proportional to area in contact and

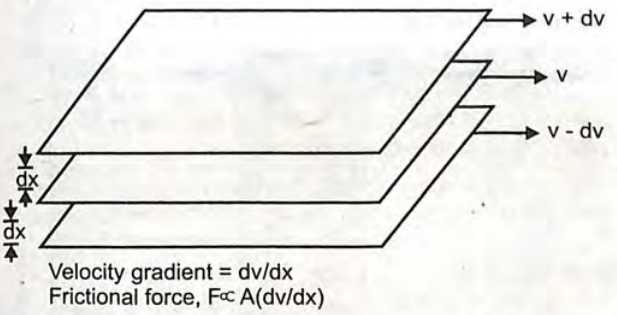


Fig.2.17 *Parallel layers of area A in a liquid*

velocity gradient, i.e.

$$f \propto A \quad \text{(area)}$$
$$\propto dv/dx \quad \text{(velocity gradient)}$$
$$\text{or } f = \eta A\, dv/dx$$

'η' is called the coefficient of viscosity and it has the unit of poise, g cm^{-1} s^{-1}, after the great scientist Poiseuille. In SI system it is Pa s or $Nm^{-2}s$ or kg $m^{-1}s^{-1}$. Commonly used unit, poise, is one tenth of the SI unit.

2.8 SOLIDS

We have seen in earlier section that a substance is in a solid state because the molecular interaction energy predominates over the disruptive thermal energy.

Covalent Solid

A wide variety of crystalline solids of nonmetals results from formation of covalent bonds between adjacent atoms. Thus a covalent solid is a giant molecule having a three dimensional network (Fig.2.18) of covalent bonds. Examples are diamond, silicon carbide, silica. These are generally very hard.

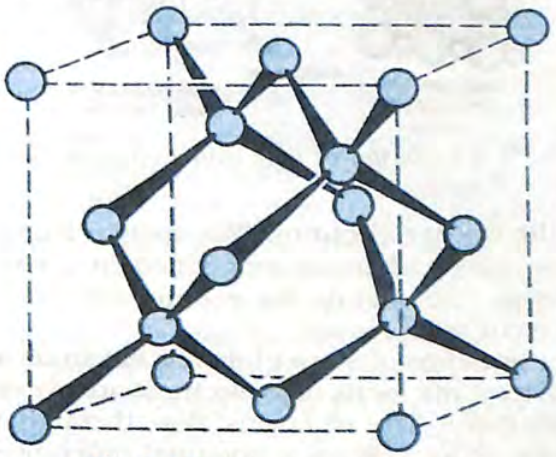


Fig.2.18 *Structure of diamond*

Ionic Solids

Ionic solids are three dimensional arrangements of cations and anions bound by coulombic forces (Fig.2.19). The crystal on the whole is electrically neutral. Such solids are characterized by high melting and boiling points. The ionic solids do not conduct electricity as ions present therein are not free to move. Examples are sodium chloride, barium oxide and calcium fluoride.

Metallic Solids

Metals are orderly collection of positive ions surrounded by and held together by free electrons, each metal atom donating one or more electrons. The metallic bonds spread over the entire crystal. The bonding is not directional. The metals are good conductors of heat and electricity. They are highly malleable and ductile. These sets of properties can be attributed to this structure of metals. Metals like sodium, crystallise in simple cubic lattice. Sodium atom releases one electron such that the crystal of sodium metal is composed of Na^+ ions

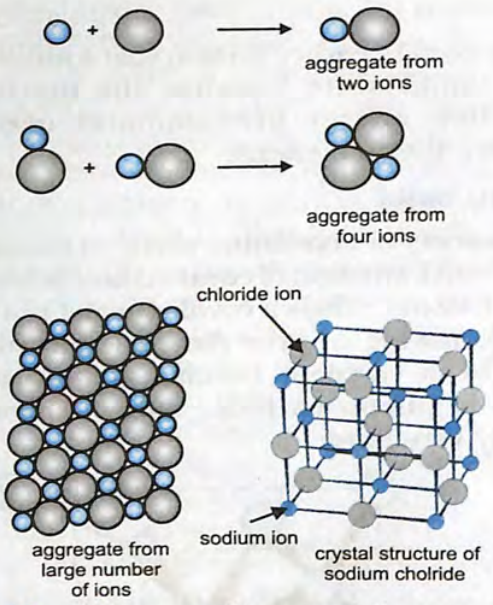


Fig.2.19 Clustering of ions and formation of ionic solids

and the valence electrons. The sodium ions can be visualized as being embedded in a sea of electrons. The metals like sodium are soft and can be cut and pressed.

The presence of a sea of mobile electrons in a metal accounts for its high electrical and thermal conductivity. The electrons flow through the network of ions when a potential difference is applied across the ends of the metal. Metals are also good conductor of heat for the same reason. Another important characteristic of metals is their lusture and colour in certain cases. This is also due to the presence of free electrons in the metals.

Molecular Solids

Many combinations of elements result into covalent molecules. These are discrete units capable of independent existence. Thus we have molecules like dihydrogen, dinitrogen, methane etc, which are called covalent compounds. They have weak molecular interaction and when crystallized lead to the formation of molecular solids. Even monatomic molecules like the noble gases, form molecular solids. These solids are characterized by low melting points.

Table 2.4 summarizes the nature of bonding for different types of solids and their characteristic properties.

2.9 INTERMOLECULAR FORCES

We have already learnt that there are weak attractive intermolecular forces that cause deviation from the ideal behaviour in gases. Solids are classified according to the type of intermolecular forces that exist in them. There is a type of force called dispersion force or London force operating between the molecules in all substances. Besides dispersion forces there are dipole- dipole, dipole-induced dipole type

Table 2.4 Bonding and Nature of Solids

Type of Solid	Constituents	Bonding	Examples	Physical Nature	M.P	B.P	Electrical Conductivit
Covalent	Atoms	Electron sharing	SiO_2(Quartz), SiC	Hard Hard	V.High (~4000K)	V.High (~5000K)	Insulators
			C (Diamond)	Hard			
			C (Graphite)	Soft			Conductor (exception)
Ionic	Ions	Coulombic	NaCl, KCl CaO, MgO	Hard but Brittle	High (~1000K)	High (~2000K)	Conductor (in molten state and in aqueous solution).
Metallic	Positive ions and electrons	Metallic	Sodium Magnesium Metals and Alloys	Ductile Malleable	High (~800K to 1000K)	High (~1500K to 2000K)	Conductor
Molecular	Simple Covalent Molecules	Molecular interactions (inter-molecular forces). Hydrogen bonding	I_2, S_8, P_4 CO_2, CCl_4	Soft	Low (~300K to 600K)	Low (~450 to 800K)	Insulators
			Starch Sucrose Water Ice	Soft	Low (~273K to 400K)	Low (~373K to 500K)	Insulators

interactions in some substances. A slightly stronger intermolecular interaction is due to hydrogen bond formation.

The low melting and boiling points of molecular solids show that the magnitude of molecular interaction energy is not very high.

2.9.1 Dispersion Forces or London Forces

According to the quantum mechanical model, as a time average the electrons are distributed symmetrically about an atom. At any given instant there may be some asymmetry in the distribution of electrons around the nucleus resulting into an instantaneous electric dipole. This produces a field which distorts the electron distribution in the neighbouring atom or molecule so that the neighbouring atom or molecule itself acquires a dipole moment (Fig.2.20). The two dipoles will attract. This is the basis of dispersion or London forces. These forces are attractive and the interaction energy due to this is proportional to $\frac{1}{r^6}$ and, therefore, these are important only at short distances (~500 pm). This also depends on the polarizability of the molecule.

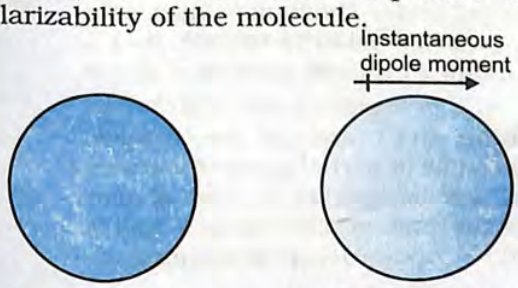

Instantaneous dipole moment
On an average the negative charge of the electrons is spread evenly
For brief periods the electrons are more on one side of an atom than another. This causes a short-lived dipole moment

Fig.2.20 *Origin of temporary dipole moment, dispersion forces*

2.9.2 Dipole-Dipole Forces

Dipole-dipole forces occur between molecules having permanent electric dipole. A bond is said to be polar, if the formation of bond leaves partial charges on the two atoms, as in the case of bond between dissimilar atoms. For example the molecule of hydrogen chloride is a polar molecule. In the bond the shared electron pair is closer to the chlorine atom because of its higher electronegativity compared to hydrogen atom. Thus as shown in Fig. 2.21 – an electric dipole results. This dipole interacts with another neighbouring dipole, hydrogen chloride polar molecule, and produces a net attractive interaction. The interaction energy is also proportional to $\frac{1}{r^6}$, where r is the distance between the polar molecules.

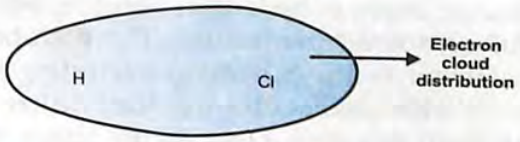


Fig.2.21 *Distribution of electron charge cloud in HCl molecules*

2.9.3 Dipole-induced Dipole Forces

Attractive forces are operative not only between the two molecules with permanent dipoles but also between a molecule having a dipole moment and a molecule without any dipole moment like CH_4. As the size of the atom increases the influence of the electric dipole on it also increases. The electron cloud of the molecule is deformed in the electric field of the permanent dipole. This causes a shift in the center of gravity of the negative charge relative to the nuclear charge and leads to the formation of an induced dipole moment (Fig.2.22). The interaction energy is also proportional to $\frac{1}{r^6}$ and also depends upon the dipole moment of the permanent dipole and the polarizability of the second molecule. Molecules of larger size have higher polarizability. Interaction between two dipolar molecules also includes additive dipole-dipole induced interactions.

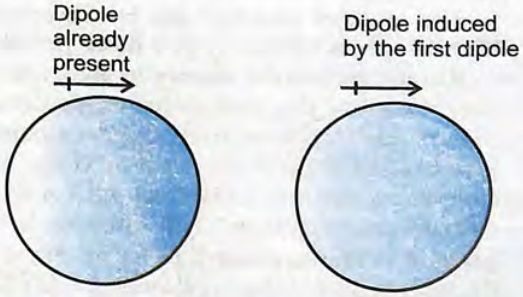


Fig.2.22 *Dipole can induce a dipole*

2.9.4 Hydrogen Bonding

Molecules having hydrogen, bonded to an

electronegative atom, can interact with another electronegative atom having a lone pair, leading to the formation of a hydrogen bond. Such bonds exist in water (Unit 11), HF, alcohols and carboxylic acids. The hydrogen bond energy varies between 10 to 100 kJ mol^{-1}. These exist mainly between molecules which have OH, NH, FH groups. Hydrogen bonding has significant effect on the physical properties of compounds.

In water, there is hydrogen bonding between two different water molecules. The high boiling point of water is due to hydrogen bonding which holds the water molecules together rather than leaving them free as in a gas. As the temperature is lowered the water converts into ice. The structure of ice is open due to hydrogen bonding which makes ice less dense than liquid water at the same temperature as shown in Fig.2.23. Ice floats on the water surface at 0°C.

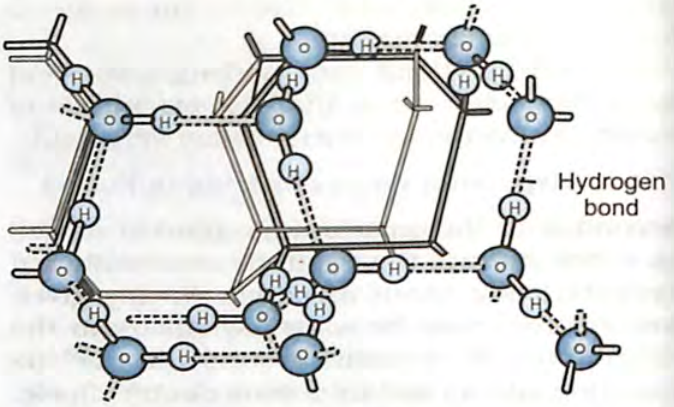


Fig.2.23 *Cage like structure of ice. Each ring contains six oxygen and six hydrogen atoms. Each hydrogen is linked by covalent bond to one oxygen atom and by hydrogen bond to another oxygen atom*

SUMMARY

The three states of matter: solid, liquid and gas are the result of competitive molecular interactions and thermal energy.

The interdependence of macroscopic variables: pressure, temperature, volume and amount gives rise to the different gas laws. Boyle's law states that under constant temperature conditions pressure of a fixed amount of gas is inversely proportional to its volume, $p \propto 1V$. Charles' law states that under isobaric condition the volume of a fixed amount of gas is directly proportional to the absolute temperature, $V \propto T$. Avogadro's law states that one mole of any substance contains 6.022×10^{23} entities and a mole of gas occupies 22.7×10^{-3} m^3 at 1 bar pressure and 273K (0°C). Dalton's law of partial pressures states that the pressure exerted by a mixture of noninteracting gases is equal to the sum of their partial pressures, $p = p_1 + p_2 + p_3$...Graham's law states that rate of diffusion of a gas is inversely proportional to square root of its density, $r \propto d^{-1/2}$, under the similar conditions of temperature and pressure.

A gas represented by the state say p_1, V_1, and T_1 changes to another state represented by p_2, V_2 and T_2; the two gaseous states are related by combined gas law $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$. Knowing any five variables, the sixth can be calculated.

The state of an ideal gas is represented by $pV = nRT$, where R is the gas constant and has the units of energy per mole per kelvin.

Kinetic molecular theory of gases provides an explanation for the different experimental observations. The postulates of the theory describes an ideal (hypothetical) gas. The theory makes assumptions that all gases consist of molecules. The molecules are point masses which do not have any interactions among themselves. The molecules are in constant ceaseless motion, colliding with each other and with the walls of the container. All collisions are elastic. The impacts on the wall result into the physical quantity called pressure. The average kinetic energy of the colliding molecules is directly proportional to its temperature, K.E. (molecule) = (3/2) kT; where k is the ratio of R to N_A (R/N_A) is called Boltzmann constant.

The behaviour of real gases points towards the inadequacies of the microscopic model. The van der Waals equation takes care of the deviations from ideal gas behaviour to some extent.

Some important properties of liquids such as vapour pressure, surface tension and viscosity are discussed.

The solids are classified according to the various interactions that bind the molecules to give ordered structure. The different types of intermolecular forces: dispersion, dipole-dipole, dipole-induced dipole and hydrogen bonding are responsible for wide variety of solids.

EXERCISES

2.1 What will be the minimum pressure required to compress 500 dm^3 of air at 1 bar to 200 dm^3 at 30°C?

2.2 A vessel of 120mL capacity contains a certain amount of gas at 35°C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180mL at 35°C. What would be its pressure?

2.3 Using the equation of state $pV=nRT$; show that at a given temperature density of a gas is proportional to gas pressure p.

2.4 At 0°C; the density of a gaseous oxide at 2 bar is same as that of nitrogen at 5 bar. What is the molecular mass of the oxide?

2.5 Pressure of 1 g of an ideal gas A at 27°C is found to be 2 bar when 2 g of another ideal gas B is introduced in the same flask at same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses.

2.6 The drain cleaner, Drainex contains small bits of aluminum which react with caustic soda to produce hydrogen. What volume of hydrogen at 20° C and one bar will be released when 0.15g of aluminum reacts?

2.7 What will be the pressure exerted by a mixture of 3.2g of methane and 4.4g of carbon dioxide contained in a 9 dm^3 flask at 27°C ?

2.8 What will be the pressure of the gas mixture when 0.5L of H_2 at 0.8 bar and 2.0L of oxygen at 0.7 bar are introduced in a 1L vessel at 27°C?

2.9 Density of a gas is found to be 5.46g/dm^3 at 27°C at 2 bar pressure. What will be its density at STP?

2.10 34.05 mL of phosphorus vapour weighs 0.0625 g at 546°C and 0.1 bar pressure. What is the molar mass of phosphorus?

2.11 A student forgot to add the reaction mixture to the round bottomed flask at 27°C but put it on the flame. After a lapse of time, he realized his mistake, using a pyrometer he found the temperature of the flask was 477°C. What fraction of air would have been expelled out?

2.12 Calculate the temperature of 4.0 moles of a gas occupying 5 dm^3 at 3.32 bar. (R = 0.083 bar dm^3 K^{-1} mol^{-1}).

2.13 Calculate the total number of electrons present in 1.4 g of nitrogen gas.

2.14. How much time would it take to distribute one Avogadro number of wheat grains, if 10^{10} grains are distributed each second ?

2.15. Calculate the total pressure in a mixture of 8 g of oxygen and 4 g of hydrogen confined in a vessel of 1 dm^3 at 27°C. R = 0.083 bar dm^3 K^{-1} mol^{-1}.

2.16. Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10m, mass 100kg is filled with helium at 1.66 bar at 27°C. (Density of air = 1.2 kg m^{-3} and R = 0.083 bar dm^3 K^{-1} mol^{-1}).

2.17 Calculate the volume occupied by 8.8g of CO_2 at 31.1°C and 1 bar pressure. R =0.083 bar L K^{-1} mol^{-1}.

2.18 2.9 g of a gas at 95°C occupied the same volume as 0.184 g of hydrogen at 17°C, at the same pressure. What is the molar mass of the gas?

2.19 Through the two ends of a glass tube of length 200 cm hydrogen chloride gas and ammonia are allowed to enter. At what distance ammonium chloride will first appear ?

2.20 For 10 minutes each, at 27°C, from two identical holes nitrogen and an unknown gas are leaked into a common vessel of 3 L capacity. The resulting pressure is 4.18 bar and the mixture contains 0.4 mol of nitrogen. What is the molar mass of the unknown gas?

2.21 Equal volumes of two gases A and B diffuse through a porous pot in 20 and 10 seconds respectively. If the molar mass of A be 80, find the molar mass of B.

2.22 Calculate the average kinetic energy of 32g methane molecules at 27°C. R = 8.314J K^{-1} mol^{-1}.

2.23 A mixture of hydrogen and oxygen at one bar pressure contains 20% by weight of hydrogen. Calculate the partial pressure of hydrogen.

2.24 What would be the SI unit for the quantity pV^2T^2 / n.

2.25 In terms of Charles' law explain why –273°C is the lowest possible temperature.

2.26 Explain the physical significance of van der Waals parameters.

2.27 Critical temperature for carbon dioxide and methane are 31.1°C and –81.9°C respectively. Which of these has stronger intermolecular forces and why?

2.28 Explain why ice has a sharp melting point where as glass melts over a range of temperature.

2.29 A manometer is connected to a gas containing bulb. The open arm reads 43.7cm where as the arm connected to the bulb reads 15.6 cm. If the barometric pressure is 743 mm mercury. What is the pressure of gas in bar ?

UNIT 3

ATOMIC STRUCTURE

Objectives

After studying this Unit, you will be able to

- describe Thomson, Rutherford, Bohr atomic models and understand the important features of the quantum mechanical model of the atom.
- understand nature of electromagnetic radiation and Planck's quantum theory, explain the photo-electric effect and describe features of atomic spectra.
- state the de Broglie relation and Heisenberg uncertainty principle, define an atomic orbital in terms of quantum numbers and state Aufbau principle, Pauli exclusion principle and Hund's rule of maximum multiplicity.
- write the electronic configurations of atoms.

"The rich diversity of chemical behaviour of different elements can be traced to the differences in the internal structure of atoms of these elements"

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter i.e., the continued subdivision of matter would ultimately yield atoms which would not be further divisible. The word "atom" has been derived from the Greek word '*atomos*' which means 'uncut-able' or 'indivisible'. These early ideas were mere speculation and there was no way to test them experimentally. They, therefore, lay dormant for a very long time and were revived again by scientists in the eighteenth century.

The atomic model of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher, in 1808. His theory, called **Dalton's atomic theory**, regarded the atom as the ultimate particle of matter (Unit-1).

Dalton's concept of the indivisibility of atom was disproved by experimental evidences obtained by scientists towards the end of the nineteenth century. It was found that atoms, tiny though they are, nonetheless have internal structure and are made up of three fundamental particles called **electron, proton** and **neutron.** The proton, a positively charged particle, is present in the highly dense central part of the atom called **nucleus**. The electron, a negatively charged particle, is present in the **extranuclear part** of the atom. The neutron, a neutral particle, is also present in the nucleus of the atom. Since an atom is electrically neutral, the number of electrons present in the extranuclear part is equal to the number of protons in the nucleus. The important properties of these fundamental particles are given in Table 3.1. Except for the hydrogen atom (which contains one electron, one proton but no neutron), the atoms of all

Table 3.1 Properties of Fundamental Particles*

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	e	-1.6022×10^{-19}	-1	9.10939×10^{-31}	0.00054	0
Proton	p	$+1.6022\times10^{-19}$	+1	1.67262×10^{-27}	1.00727	1
Neutron	n	0	0	1.67493×10^{-27}	1.00867	1

other elements, including deuterium and tritium (isotopes of hydrogen) contain all the three fundamental particles: electrons, protons and neutrons. Furthermore, the internal structure of different atoms differ and the rich diversity of chemical behaviour of elements can be traced to the different internal structures of their atoms.

3.1 EARLIER ATOMIC MODELS

Dalton's atomic theory regarded atom as indivisible. Discovery of sub-atomic particles necessitated the revision of this theory. Atomic models were, therefore, proposed to explain the structure of atom. Different atomic models are the pictures of the structure of atom proposed from time to time. Two of the earlier models were those proposed by J.J. Thomson and Ernest Rutherford, respectively.

3.1.1 Thomson Model of Atom

J.J.Thomson, the discoverer of electron, proposed in 1898 a model in which he assumed an atom to consist of a uniform sphere (radius approx. 10^{-10}m) of positive electricity (positive charge) with electrons embedded into it in such a way as to give the most stable electrostatic arrangement (Fig.3.1). In this model, the atom is visualized as a pudding or cake of positive charge with raisins (electrons) embedded into it. This model is, therefore, sometimes called the **'raisin pudding'** model. An important feature of this model is that the *mass of the atom is considered to be evenly spread over the atom.* Thomson was awarded the 1906 Nobel Prize in Physics.

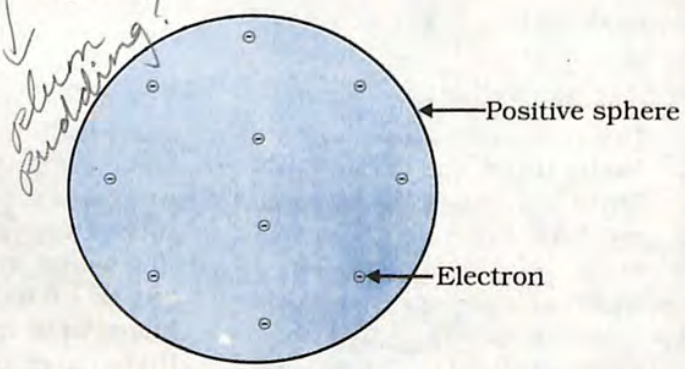


Fig.3.1 *Thomson model of atom*

This model of atom could account for the electrical neutrality of atom, but it could not explain the results of gold foil scattering experiment carried out by Rutherford.

Ernest Rutherford was born in New Zealand but went to Cambridge University in England to pursue his Ph.D. in 1895. In 1899, he moved to McGill University in Canada. In 1907, Rutherford moved from Canada to Manchester University in England, and there he performed the experiments that gave us the modern view of the atom. Rutherford was awarded the 1908 Nobel Prize in Chemistry for his investigations on the chemistry of radioactive substances. In a series of experiments analyzing the radiation emitted by elements such as uranium, he discovered that such radiation consisted of three components, alpha, beta and gamma rays.

Ernest Rutherford (1871-1937)

* *Fundamental particles such as protons and neutrons are believed to be made up of various combinations of elementary particles called* ***quarks****. First proposed by Murray Gellmann in 1963, quarks are believed to have fractional charges and other properties such as flavour and colour.*

3.1.2 Rutherford Nuclear Model of Atom

The distribution of charges proposed by Thomson in his model was tested by Ernest Rutherford in 1909 by using subatomic projectiles to bombard a target of atoms. These projectiles, called **alpha (α) particles**, were identified as one of the products of radioactivity. Alpha particles are high energy, positively charged helium ions emitted during radioactive decay of unstable elements such as uranium. An alpha particle has charge +2 and mass 4 u. Rutherford's famous **alpha particle-scattering experiment** is represented in Fig.3.2. A stream of high energy α-particles from a radioactive source was directed at a thin foil (thickness~100 nm) of gold metal. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever an α-particle struck the screen, a tiny flash of light was produced at that point.

According to Thomson Model of atom, the mass of each gold atom in the foil should have been spread evenly over the entire atom. Rutherford knew that alpha particles had enough energy to pass directly through such a uniform distribution of mass. He expected the particles to slow down and change direction only by a small angle as they passed through the foil. The results of Rutherford's experiment were, however, quite unexpected. He observed that :

(i) most of the α-particles passed through the gold foil undeflected.

(ii) a small fraction of the alpha particles was deflected by small angles.

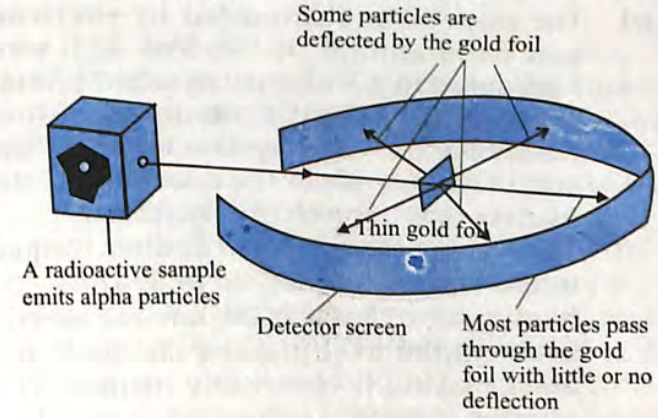
(iii) a very few alpha particles (1 in 20,000) bounced back i.e., were deflected by nearly 180°.

On the basis of these observations, Rutherford drew the following conclusions regarding the structure of atom:

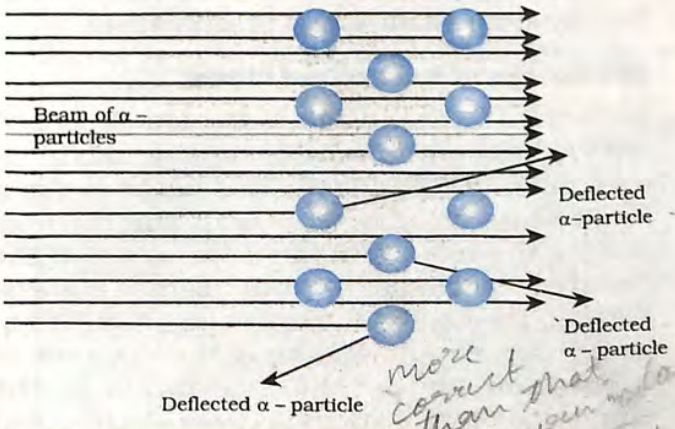
(i) Most of the space in the atom is empty as most of the α-particles passed through the foil.

(ii) A few positively charged α-particles are deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had thought. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α-particles. This very small portion of the atom was called **nucleus** by Rutherford.

(iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m while that of nucleus is 10^{-15} m. One can appreciate this difference in size by realising that if a cricket ball represents a nucleus, then radius of the atom would be about 5 km.


Some particles are deflected by the gold foil
Thin gold foil
A radioactive sample emits alpha particles
Detector screen
Most particles pass through the gold foil with little or no deflection

A Rutherford's scattering experiment



B. Schematic molecular view of the gold foil

Fig.3.2 *Schematic view of Rutherford's scattering experiment. When a beam of alpha (α) particles is "shot" at a thin gold foil, most of them pass through without much effect. Some, however, are deflected.*

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model :

(a) An atom consists of a tiny positively charged nucleus at its centre.

(b) The positive charge of the nucleus is due to protons. The mass of the nucleus, on the other hand, is due to protons and some other neutral particles each having mass nearly equal to the mass of proton. This neutral particle, called neutron, was discovered later on by chadwick in 1932. Protons and neutrons present in the nucleus are collectively also known as nucleons. The total number of nucleons is termed as **mass number (A)** of the atom.

(c) The nucleus is surrounded by electrons that move around the nucleus with very high speed in circular paths called **orbits**. Thus, Rutherford's model of atom resembles the solar system in which the sun plays the role of the nucleus and the planets that of revolving electrons.

(d) The number of electrons in an atom is equal to the number of protons in it. Thus, the total positive charge of the nucleus exactly balances the total negative charge in the atom making it electrically neutral. The number of protons in an atom is called its atomic number **(Z)**.

(e) Electrons and the nucleus are held together by electrostatic forces of attraction.

Drawbacks of Rutherford Model

Rutherford nuclear model of an atom described above was established on the basis of α - scattering experiment. This model is like a small scale solar system with the nucleus playing the role of the massive sun and the electrons being similar to the lighter planets. Further, the coulomb force (kq_1q_2/r^2 where q_1 and q_2 are the charges, r is the distance of separation of the charges and k is the proportionality constant) between electron and the nucleus is mathematically similar to the gravitational force $\left(G.\frac{m_1m_2}{r^2}\right)$ where m_1 and m_2 are the masses, *r* is the distance of separation of the masses and G is the gravitational constant between a planet and the sun. When classical mechanics * is applied to the solar system, it shows that the planets describe well-defined orbits around the sun. The theory can also calculate precisely the planetary orbits and these are in agreement with the experimental measurements. The similarity between the solar system and nuclear model suggests that electrons should move around the nucleus in well defined orbits. However, when a body is moving in an orbit, it undergoes acceleration (even if the body is moving with a constant speed in an orbit, it must accelerate because of changing direction). So an electron in the nuclear model describing planet like orbits is under acceleration. According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom if the motion of an electron is described on the basis of the classical mechanics and electromagnetic theory. You may ask that since the motion of electrons in orbits is leading to the instability of the atom, then why not consider electrons as stationary around the nucleus. If the electrons were stationary, electrostatic attraction between the dense nucleus and the electrons would pull the electrons toward the nucleus to form a miniature version of Thomson atom.

Another serious drawback of the Rutherford model is that it says nothing about the electronic structure of atoms i.e., how the electrons are distributed around the nucleus and what are the energies of these electrons.

3.2 DEVELOPMENTS LEADING TO THE BOHR MODEL OF ATOM

The first major attempt to improve Rutherford model of atom was made by Niels Bohr. Two developments played a major role in the formulation of the Bohr model of the atom. These were :

(i) Dual behaviour of the electromagnetic radiation which means that light has both particle and wave-like properties, and

* *Classical mechanics is a theoretical science based on Newton's laws of motion. It specifies the laws of motion of macroscopic objects.*

(ii) Experimental results regarding atomic spectra which can be explained only by assuming quantized electronic energy levels in atoms.

3.2.1 Nature of Electromagnetic Radiation

Radiation is the emission and transmission of energy through space in the form of waves. James Maxwell in 1873, showed that visible light consists of electromagnetic waves i.e., waves consisting of oscillating electric and magnetic fields. These two field components have the same wavelength and frequency and travel in planes perpendicular to each other and also perpendicular to the direction of propagation of the electromagnetic wave as shown in Fig.3.3. It is now well known that there are many types of electromagnetic radiation and the visible light is one of them.

In vacuum, all types of electromagnetic

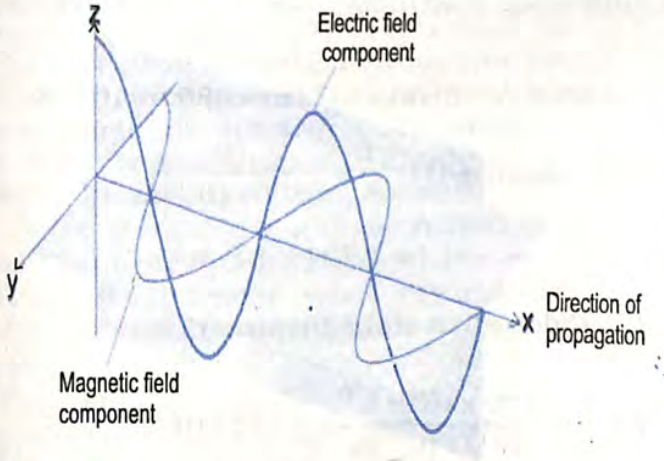


Fig.3.3 *The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.*

radiation, regardless of their wavelength, travel at the same speed i.e., 3.00×10^8 m s^{-1}. This speed is called the speed of light* and is given the symbol c. The frequency of the radiation, ν (nu) is the number of waves that pass a given point in a second and has the unit s^{-1}, also called Hertz (Hz) after Heinrich Hertz. For a given type of radiation, the wavelength λ (lambda), the frequency ν and speed of light c are related by the equation.

$$\lambda \nu = c \qquad (3.1)$$

Another quantity called wave number ($\bar{\nu}$) is often used to characterize the waves : $\bar{\nu} = \frac{1}{\lambda}$.

Wave number is the number of wavelengths per unit of length. Its unit is the reciprocal of wavelength unit i.e., it is often given in cm^{-1} or m^{-1}.

Fig.3.4 shows various types of electromagnetic radiation which differ from one-another in wavelength (or frequency). These constitute the so-called electromagnetic spectrum. Different regions of the spectrum are identified by different names. Some examples are: radio-frequency region, around 10^6 Hz, used for broadcasting; microwave region, around 10^{10} Hz, used for radar; infrared region, around 10^{13} Hz, is the heat radiation; and ultraviolet region, around 10^{16} Hz, a component of Sun's radiation. The small portion (around 10^{15} Hz) is what is ordinarily called visible light. It is the only part which our eyes can see (or detect). Special instruments are needed to detect non-visible types of electromagnetic radiation.

Example 3.1

The Vividh Bharati station of All India Radio, Delhi broadcasts on a frequency of 1,368 kHz (kilo hertz). Calculate the wavelength of the electromagnetic radiation emitted by the transmitter.Which part of the electromagnetic spectrum does it belong to ?

Solution

The wavelength, λ, is equal to c/ν where c is the speed of electromagnetic radiation in vacuum and ν is the frequency. Substituting the given values, we have

$$\lambda = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1368 \text{ kHz}} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1368 \times 10^3 \text{ s}^{-1}} = 219.3 \text{ m}$$

This is a characteristic radiowave wavelength.

* *The speed of light in air is slightly less than its speed in vacuum but the difference is so small that it can be ignored in most cases.*

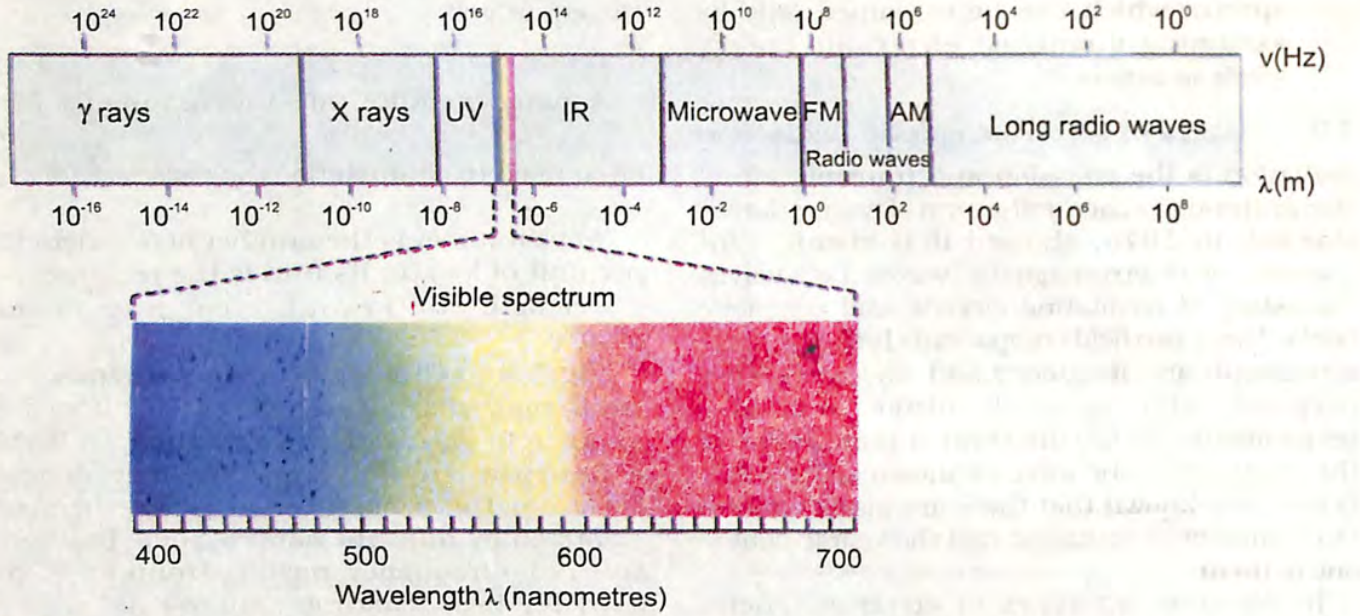


Fig.3.4 *The spectrum of electromagnetic radiation. The visible region is only a small part of the entire spectrum (a) Overall spectrum (b) Visible region.*

Example 3.2

The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz). [1nm = 10^{-9} m.]

Solution

Frequency of violet light

$$\nu = \frac{c}{\lambda} = \frac{3.00\times10^{8}\ \text{m s}^{-1}}{400\times10^{-9}\ \text{m}} = 7.50\times10^{14}\ \text{Hz}$$

Frequency of red light

$$\nu = \frac{c}{\lambda} = \frac{3.00\times10^{8}\ \text{m s}^{-1}}{750\times10^{-9}\ \text{m}} = 4.00\times10^{14}\ \text{Hz}$$

Example 3.3

Calculate (a) wave number and (b) frequency of yellow radiation having wavelength of 5800 Å.

Solution

(a) Calculation of wave number $\bar{\nu}$

$$\lambda = 5800\ \text{Å} = 5800\times10^{-8}\ \text{cm} = 5800\times10^{-10}\ \text{m}$$

$$\text{Wave number } (\bar{\nu}) = \frac{1}{\lambda} = \frac{1}{5800\times10^{-10}\text{m}}$$

$$= 1.724\times10^{6}\ \text{m}^{-1}.$$

(b) Calculation of the frequency ν

$$\nu = \frac{c}{\lambda} = \frac{3.00\times10^{8}\text{m s}^{-1}}{5800\times10^{-10}\text{m}} = 5.172\times10^{14}\text{s}^{-1}$$

Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomena such as diffraction* and interference** can be explained by the wave nature of the electromagnetic radiation. However, experimental observations such as emission of radiation from a hot body and photoelectric effect cannot be explained on this basis.

When solids are heated they emit radiation over a wide range of wavelengths. For example,

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* *Diffraction is the bending of wave around an obstacle.*

** *Interference is the combining of two waves of the same frequency to give a wave whose disturbance at each point in space is the algebraic or vector sum of the disturbances at that point resulting from each interfering wave.*

Max Planck
(1858 - 1947)

Max Planck, a German physicist, received his Ph.D in theoretical physics from the University of Munich in 1879. In 1888, he was appointed Director of the Institute of Theoretical Physics at the University of Berlin. Planck was awarded the Nobel Prize in Physics in 1918 for his quantum theory. Planck also made significant contributions in thermodynamics and other areas of physics.

when an iron rod is heated in a furnace, it first turns a dull red and then progressively becomes more and more red as the temperature increases. As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. In terms of frequency, it means that the radiation emitted goes from a lower frequency to a higher frequency as the temperature increases. The red colour lies is in the lower frequency region while blue colour belongs to the higher frequency region of the electromagnetic spectrum. The ideal body, which emits and absorbs all frequencies, is called a **blackbody** and the radiation emitted by this body is called **blackbody radiation**. The exact frequency distribution of the emitted radiation (i.e. intensity versus frequency curve of the radiation) from a black body depends upon its temperature.

The above experimental results cannot be explained satisfactorily on the basis of the wave theory of light. In 1900, Max Planck provided an explanation for this behaviour. He said that atoms and molecules could emit (or absorb) energy only in discrete quantities and not in any arbitrary amount as it was believed till then. Planck gave the name **quantum** to the smallest quantity of energy that can be emitted (or absorbed) in the form of electromagnetic radiation. The energy of a quantum of radiation is proportional to its frequency and is expressed as

$$E = h\nu \qquad (3.2)$$

The proportionality constant, h, is known as **Planck constant** and has the value 6.626×10^{-34} J s.

According to Planck's theory, energy is always emitted in integral multiples of hν, for example hν, 2hν, 3hν etc. Planck, however, could not explain why energies should be quantized in this manner. However, with this assumption, Planck could explain the distribution of intensity in radiation from a black body as a function of frequency at different temperatures.

Photoelectric Effect

Experiments show that electrons are ejected from the surface of certain metals (like Cs, K and Rb) when they are exposed to light of appropriate frequency (Fig.3.5). This phenomenon is known as **photoelectric effect**.

According to the wave theory of light, both the number of electrons ejected and their energies should depend on the intensity of the incident light. In practice, it is found that while the number of electrons ejected does depend on the intensity of the incident light, their energies do not. Einstein was able to explain the photoelectric effect by making the most extraordinary assumption. He suggested that light consists of streams of particles called photons which move with the speed of light. Using Planck's quantum theory of radiation as a starting point, Einstein deduced that each photon must possess energy E, given by $E = h\nu$ where ν is the frequency of light.

Shooting a beam of light onto a metal surface can, therefore, be viewed as shooting a beam of particles – the photons. When a photon strikes an electron in the atom of the metal with sufficient energy, the electron may be knocked out of the atom. The more energetic the photon is, the more energy it transfers to the electron and the greater the energy of the ejected electron. A more intense beam of light consists of a large number of photons, consequently the number of electrons ejected is also larger as compared to an experiment in which a beam of weaker intensity of light is employed.

Albert Einstein, a German born American physicist, is regarded by many as one of the two great physicists the world has known (the other is Isaac Newton). His three research papers (on special relativity, Brownian motion and the photoelectric effect) which he published in 1905, while he was employed as a technical assistant in a Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.

Albert Einstein (1879 - 1955)

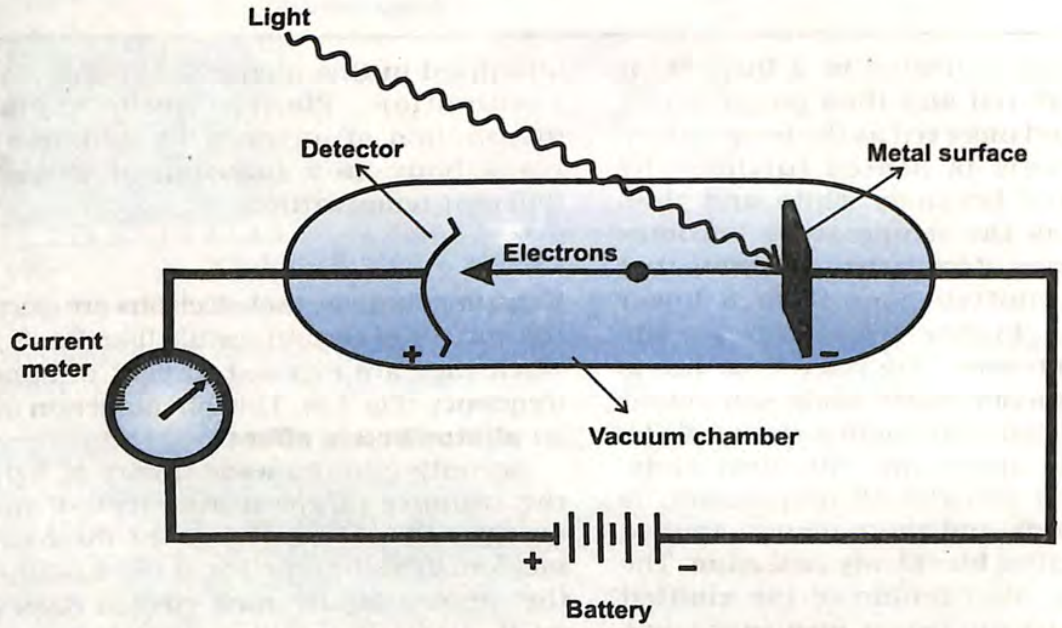

Fig.3.5 *Equipment for studying the photoelectric effect. Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.*

Threshold frequency (ν_0) and kinetic energy of photoelectrons

For each metal, there is a characteristic minimum frequency– the threshold frequency (ν_0) — below which the photoelectric effect does not occur. Red light ($\nu = 4.3 - 4.6 \times 10^{14}$ Hz), for example, of any intensity may shine on a piece of potassium for hours but no photoelectrons will be released. But as soon as even a very weak yellow light ($\nu = 5.1 - 5.2 \times 10^{14}$ Hz) shines on potassium, the photoelectric effect is observed. The threshold frequency, ν_0 for potassium is 5×10^{14} Hz. For photoelectric effect to occur, the striking photon should have frequency more than that of the threshold frequency. If a photon of frequency (ν) strikes a metal atom whose threshold frequency is ν_0 then photoelectrons will be emitted only if $\nu > \nu_0$. Since the striking photon has energy equal to $h\nu$ and the minimum energy required to eject electron is $h\nu_0$ (also called work function, W_0) then $h\nu - h\nu_0$ is transformed as the kinetic energy of the photoelectron ($\frac{1}{2} m_e v^2$) where m_e is the mass of electron and v its velocity. Since total energy has to be conserved, one may write **Einstein's equation** as

$h\nu - h\nu_0 = \frac{1}{2} m_e v^2$ = kinetic energy of electron

Table 3.2 Values of Work Function (W_0) for a Few Metals

	Li	Na	K	Mg	Cu	Ag
W_0/eV	2.42	2.3	2.25	3.7	4.8	4.3

Dual Behaviour of Electromagnetic Radiation

The particle nature of light posed a dilemma for scientists. On the one hand, it could explain the

photoelectric effect satisfactorily but on the other hand, this was not consistent with the known wave behaviour of light which could account for the phenomena of interference and diffraction. The only way to resolve the dilemma was to accept the idea that light possesses both particle and wave-like properties, i.e., light has dual behaviour. Depending on the experiment, we find that light behaves either as a wave or as a stream of particles. Whenever radiation interacts with matter, it displays particle like properties, in contrast to the wavelike properties (interference and diffraction) it exhibits when it propagates. This concept was totally alien to the way the scientists thought about matter and radiation and it took them a long time to become convinced of its validity. It turns out, as you shall see later, that some microscopic particles like electrons also exhibit this wave-particle duality.

Example 3.4

Calculate the energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz.

Solution

Energy (E) of one photon is given by the expression

$E = h\nu$

$h = 6.626 \times 10^{-34}$ J s

$\nu = 5 \times 10^{14}$ s^{-1} (given)

$E = (6.626 \times 10^{-34}$ J s) $\times$ $(5 \times 10^{14}$ s$^{-1})$

$= 3.313 \times 10^{-19}$ J

Energy of one mole of photons

$= (3.313 \times 10^{-19}$ J) $\times$ $(6.022 \times 10^{23}$ mol$^{-1})$

$= 199.51$ kJ mol^{-1}

Example 3.5

A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.

Solution

Power of the bulb = 100 watt = 100 J s^{-1}

Energy of one photon $E = h\nu = hc/\lambda$

$$= \frac{6.626 \times 10^{-34}\ \text{J s} \times 3 \times 10^{8}\ \text{m s}^{-1}}{400 \times 10^{-9}\ \text{m}} = 4.969 \times 10^{-19}\ \text{J}$$

No. of photons emitted

$$= \frac{100\ \text{J s}^{-1}}{4.969 \times 10^{-19}\ \text{J}} = 2.012 \times 10^{20}\ \text{s}^{-1}$$

Example 3.6

When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of 1.68×10^{5} J mol^{-1}. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted ?

Solution

The energy (E) of a 300 nm photon is given by

$$h\nu = hc/\lambda = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.0 \times 10^{8}\ \text{m s}^{-1}}{300 \times 10^{-9}\ \text{m}}$$

$= 6.626 \times 10^{-19}$ J

The energy of 1 mole of photons

$= 6.626 \times 10^{-19}$ J $\times$ 6.022×10^{23} mol^{-1}

$= 3.99 \times 10^{5}$ J mol^{-1}

The minimum energy needed to remove a mole of electrons from sodium

$= (3.99 - 1.68)\ 10^{5}$ J mol^{-1} $= 2.31 \times 10^{5}$ J mol^{-1}

The minimum energy for one electron

$$= \frac{2.31 \times 10^{5}\ \text{J mol}^{-1}}{6.022 \times 10^{23}\ \text{electrons mol}^{-1}} = 3.84 \times 10^{-19}\ \text{J}$$

This corresponds to the wavelength

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.0 \times 10^{8}\ \text{m s}^{-1}}{3.84 \times 10^{-19}\ \text{J}}$$

= 517 nm (This corresponds to green light)

Example 3.7

The threshold frequency ν_0 for a metal is 7.0×10^{14} s^{-1}. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.0 \times 10^{15}$ s^{-1} hits the metal.

Solution

According to Einstein's equation

Kinetic energy = $\frac{1}{2} m_e v^2 = h(\nu - \nu_0)$

$= (6.626 \times 10^{-34}$ J s) $(1.0 \times 10^{15}$ s^{-1} - 7.0×10^{14} s$^{-1})$

$= (6.626 \times 10^{-34}$ J s) $(10.0 \times 10^{14}$ s^{-1} - 7.0×10^{14} s$^{-1})$

$= (6.626 \times 10^{-34}$ J s) $\times$ $(3.0 \times 10^{14}$ s$^{-1})$

$= 1.988 \times 10^{-19}$ J

3.2.2 Evidence for the Quantized* Electronic Energy Levels : Atomic Spectra

When a ray of light is passed through a prism, it gets refracted. The wave with a shorter wavelength bends more than the one with a longer wavelength. Since ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called **spectrum**. The red colour with the longest wavelength is deviated the least while the violet with the shortest wavelength is deviated the most. The spectrum of white light, that we can see, ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz. This spectrum is called **continuous spectrum**– continuous because violet merges into blue, blue into green and so on. A similar spectrum is produced when a rainbow forms in the sky. Remember that visible light is just a small portion of the electromagnetic radiation (3.2.1). When electromagnetic radiation interacts with matter, energy is exchanged and atoms and molecules may absorb this energy. In returning to their normal more stable lower energy states, the atoms and molecules may then emit radiation in various parts of the electromagnetic spectrum.

The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum.** Atoms, molecules or ions that have absorbed radiation are "**excited**". To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

An **absorption spectrum** is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelengths which correspond to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other

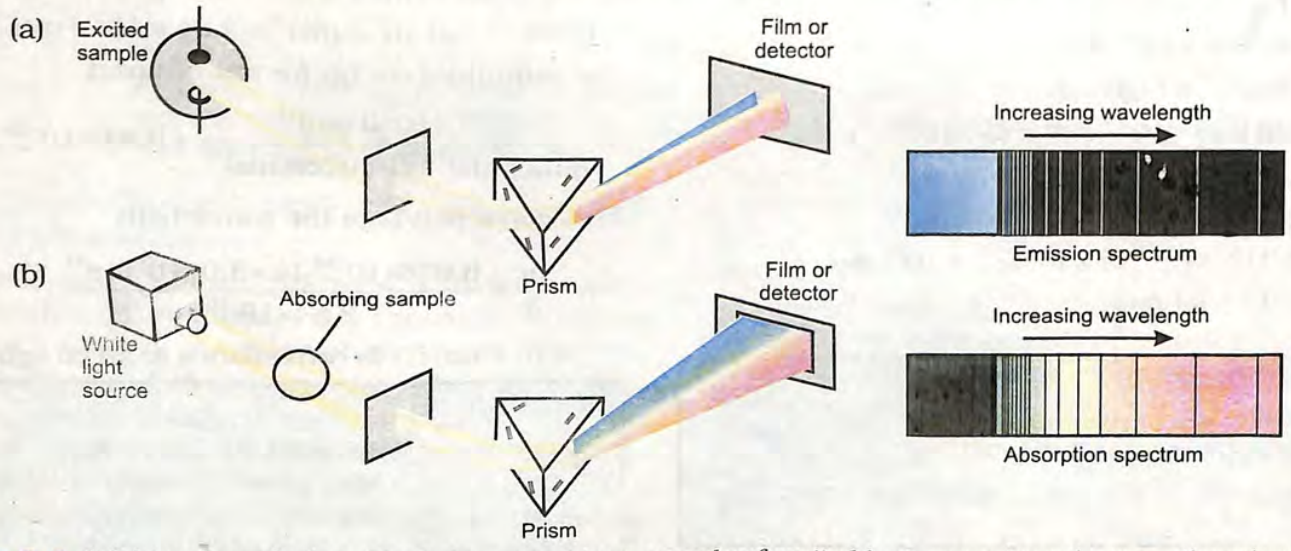

Fig.3.6 ***(a) Atomic emission.*** *The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed thruogh a prism and separated into certain discrete wavelengths. Thus an emission specturm, which is a photographic recording of the separated wavelenghts is called a line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the specturm.* ***(b) Atomic absorption.*** *When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a). The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.*

* *The restriction of any property to discrete values is called quantization.*

hand, do not show a continuous spread of wavelength from red to violet; rather they emit light only at specific wavelengths. Such spectra are called **line spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig.3.6).

Line emission spectra are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms as much as finger prints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter.

Elements like rubidium (Rb), caesium (Cs), thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

Hydrogen Spectrum

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers. Balmer showed in 1885 on the basis of experimental observations that if spectral lines are expressed in terms of wave number ($\bar{\nu}$), then the visible lines of the hydrogen spectrum obey the following formula:

$$\bar{\nu} = 109{,}677 \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \text{cm}^{-1} \qquad (3.3)$$

where n is an integer equal to or greater than 3 (i.e. n = 3,4,5, ...)

The lines described by this formula are called the Balmer series. The Balmer series of lines are the only lines in the hydrogen spectrum which appear in the visible region of the electromagnetic spectrum. The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression:

$$\bar{\nu} = 109{,}677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1} \qquad (3.4)$$

where $n_1 = 1, 2 \ldots$.

$n_2 = n_1 + 1, n_1 + 2 \ldots$

The value 109,677 cm^{-1} is called the **Rydberg constant** for hydrogen. The first five series of lines that correspond to $n_1 = 1, 2, 3, 4, 5$ are known as Lyman, Balmer, Paschen, Brackett and Pfund series, respectively. Table 3.3 shows these series of transitions in the hydrogen spectrum. Fig 3.7 shows the Lyman, Balmer and Paschen series of transitions for hydrogen atom.

Table 3.3 The Spectral Lines for Atomic Hydrogen

Series	n_1	n_2	Spectral Region
Lyman	1	2,3...	Ultraviolet
Balmer	2	3,4...	Visible
Paschen	3	4,5...	Infrared
Brackett	4	5,6...	Infrared
Pfund	5	6,7...	Infrared

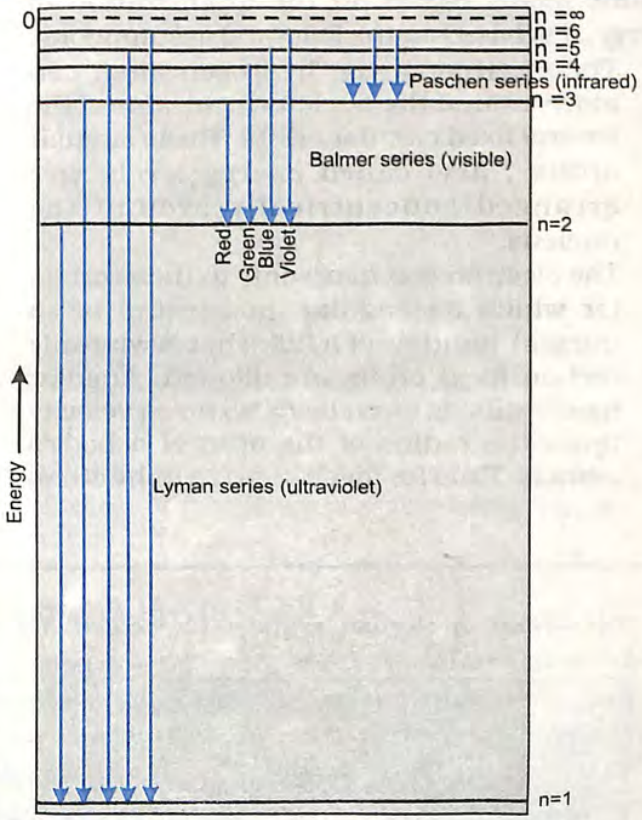

Fig.3.7 *Transitions of the electron in the hydrogen atom (The diagram shows the Lyman, Balmer and Paschen series of transitions).*

Of all the elements, hydrogen has the simplest line spectrum. Line spectra become more and more complex for heavier atoms. There are, however, certain features which are common to all line spectra viz. (i) line spectrum of each element is unique; and (ii) there is regularity in the line spectrum of each element. What are the reasons for these common features? Have they something to do with the electronic structure of atoms of these elements? These are the questions that need to be answered and as we shall find later, the answers to these questions provided the key to understanding electronic structure of atoms of these elements.

3.3 Bohr Model of Atom

Niels Bohr in 1913 proposed a model of the hydrogen atom that not only did away with the problem of Rutherford's unstable atom but also satisfactorily explained the line spectrum of hydrogen element. Bohr model was the first atomic model based on the quantization of energy. It is based on the following assumptions:

1. The electron in the hydrogen atom can move around the nucleus in any one of the several fixed circular orbits. These circular orbits , also called energy levels, are arranged concentrically around the nucleus.
2. The electron can move only in those orbits for which its angular momentum is an integral multiple of $h/2\pi$. That is why only certain fixed orbits are allowed. Angular momentum is given by mass times velocity times the radius of the orbit of a body's motion. Thus for an electron in Bohr atom,

$$m_e v r = \frac{nh}{2\pi} \qquad (3.5)$$

where n= 1, 2, 3....

3. The electron has a definite energy, characteristic of the orbit in which it is moving. As long as the electron remains in an orbit it does not loose energy. These orbits or energy levels, therefore, are also called stationary* orbits. The orbit with (n=1) is closest to the nucleus and an electron in this level has the lowest possible energy since it is closest to the positive charge of the nucleus. With increasing distance from the nucleus, the radius of the orbit and the energy of an electron in the orbit increase. Energy will have to be supplied to move the electron from a lower energy orbit to a higher energy orbit. An electron cannot have an energy that would place it between the two permissible orbits.
4. When an electron moves from a higher energy (E_2) orbit to a lower energy (E_1) orbit; the energy ΔE (= $E_2 - E_1$) is emitted in the form of a photon of frequency ν such that

$$\Delta E = E_2 - E_1 = h\nu \qquad (3.6)$$

If the electron is to be raised from energy state 1 to 2, the same quantity of energy must be absorbed. From Bohr model, one can calculate the energy E_n of an electron in an orbit n. This is given by the expression

$$E_n = \frac{\left(-2.18\times10^{-18}\,J\right)}{n^2}\,atom^{-1} \quad n = 1,2,3.... \qquad (3.7)$$

$$= -\frac{(13.595\ eV)}{n^2}\,atom^{-1} \qquad (3.8)$$

Niels Bohr, a Danish physicist received his Ph.D: from the University of Copenhagen in 1911. He then spent a year with J.J. Thomson and Ernest Rutherford in England. In 1913, he returned to Copenhagen where he remained for the rest of his life. In 1920 he was named Director of the Institute of theoretical Physics. After first World War, Bohr worked energetically for peaceful uses of atomic energy. He received the first Atoms for Peace award in 1957. Bohr was awarded the Nobel Prize in Physics in 1922.

Niels Bohr (1885–1962)

The word stationary orbit here means that the energy of the electron in the orbit is stationary i.e., it does not change with time.

Angular Momentum

Just as linear momentum is the product of mass (m) and linear velocity (v), angular momentum is the product of moment of inertia (I) and angular velocity (ω). For an electron of mass m_e, moving in a circular path of radius r around the nucleus,

angular momentum = I × ω

Since $I = m_e r^2$, and $\omega = v/r$ where v is the linear velocity,

∴angular momentum = $m_e r^2 \times v/r = m_e vr$

Further, one can also calculate the radius of each circular orbit from the expression

$r_n = 0.529\ \text{Å}\ (n^2)$ where n = 1,2,3... (3.9)

One can see that as n increases, r_n also increases indicating a greater separation between the orbit and the nucleus. The radius of the first orbit r_1, called the **Bohr radius**, (*n* =1) is 0.529 Å (52.9 pm).

Bohr model is also applicable to ions such as He^+, Li^{2+} etc. which, like hydrogen atom, contain one electron and are, therefore, known as hydrogen like systems. For such systems equations 3.8 and 3.9 become

$$En = \frac{-(13.595\ \text{eV})Z^2}{n^2}\ \text{atom}^{-1} \qquad (3.10)$$

and $$r_n = \frac{0.529\ \text{Å}\left(n^2\right)}{Z} \qquad (3.11)$$

where Z is the atomic number and has values of 2 and 3 for He^+ and Li^{2+}, respectively.

3.3.1 Explanation of the Emission Spectrum of Hydrogen

Bohr theory of the hydrogen atom enables us to explain its line spectra. Radiation (energy) is absorbed by the atom when the electron moves from a lower energy orbit (characterized by a smaller n value) to a higher energy orbit (characterized by a larger n value). Conversely, radiation (energy) is emitted when the electron moves from a higher energy orbit to a lower energy orbit.

Let us now apply equation 3.7 to the emission process in a hydrogen atom. Suppose that the electron is in an excited state with $n = n_2$. During emission, the electron drops to a lower energy state with $n = n_1$. The difference between the energies of the initial and final states is given by ΔE where

$$\Delta E = E_{n_2} - E_{n_1}$$

Using equation 3.7

$$E_{n_2} = \frac{(-2.18 \times 10^{-18}\ \text{J})}{n_2^2}$$

$$E_{n_1} = \frac{(-2.18 \times 10^{-18}\ \text{J})}{n_1^2}$$

$$\Delta E = E_{n_2} - E_{n_1}$$

$$\Delta E = \frac{(-2.18 \times 10^{-18}\ \text{J})}{n_2^2} - \frac{(-2.18 \times 10^{-18}\ \text{J})}{n_1^2}$$

Since this transition results in the emission of a photon of frequency ν with energy hν, we can write

$$E = h\nu = \left(2.18 \times 10^{-18}\ \text{J}\right)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (3.12)$$

What does the negative electronic energy (E_n) for hydrogen atom mean?

The energy of the electron in a hydrogen atom has a negative sign for all possible orbits (eq. 3.7). What does this negative sign convey? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting n equal to infinity in the equation (3.7) so that $E_\infty = 0$. As the electron gets closer to the nucleus (as n decreases), E_n becomes larger in absolute value and more and more negative. The most negative energy value is given by n=1 which corresponds to the most stable orbit. We call this the ground state.

Since $h = 6.626 \times 10^{-34}$ J s

$$\nu = \left(\frac{(2.18\times10^{-18}\text{J})}{6.626\times10^{-34}\text{J s}}\right)\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$\nu = (3.29\times10^{15})\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\text{s}^{-1} \quad (3.13)$$

In terms of wave number ($\bar{\nu}$), we have

$$\bar{\nu} = \frac{\upsilon}{c} = \frac{3.29\times10^{15}\ \text{s}^{-1}}{3\times10^{10}\ \text{cm s}^{-1}}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$\bar{\nu} = 109677\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\text{cm}^{-1} \quad (3.14)$$

The above equation is the same as the Rydberg equation 3.4 deduced from the experimental data. Remember that each spectral line in the emission spectrum corresponds to a particular transition in a hydrogen atom. When we study a large number of hydrogen atoms, we observe all possible transitions and hence the corresponding spectral lines. The brightness of a spectral line depends on how many photons of the same wavelength (or frequency) are emitted.

Example 3.8

What are the frequency and wavelength of a photon emitted during a transition from the n = 5 state to the n = 2 state in the hydrogen atom ?

Solution

Since $n_1 = 2$ and $n_2 = 5$, this transition gives rise to a spectral line in the Balmer series. From eq. (3.12) we have:

$$\Delta E = 2.18\times10^{-18}\text{J}\left[\frac{1}{2^2}-\frac{1}{5^2}\right] = 4.58\times10^{-19}\text{J}$$

The frequency of the photon is given by

$$\nu = \frac{\Delta E}{h} = \frac{4.58\times10^{-19}\text{J}}{6.62\times10^{-34}\text{J s}} = 6.91\times10^{14}\text{s}^{-1}, \text{ and}$$

$$\lambda = \frac{c}{\nu} = \frac{3.0\times10^{8}\text{m s}^{-1}}{6.91\times10^{14}\text{s}^{-1}} = 434\ \text{nm}$$

Example 3.9

Calculate the energy associated with the first orbit of He^+. What is the radius of this orbit?

Solution

According to the equation (3.10)

$$E_n = \frac{-(13.595\ \text{eV})Z^2}{n^2}\ \text{atom}^{-1}$$

n = 1

Z = 2 for He^+

$$E_1 = \frac{-13.595\,\text{eV}\times4}{1^2} = -54.380\,\text{eV}$$

The radius of the orbit is given by equation (3.11)

$$r_n = \frac{(0.529\ \text{Å})n^2}{Z}$$

Since n = 1 and Z = 2

$$r_1 = \frac{0.529\times1^2}{2} = 0.2645\ \text{Å}$$

3.3.2 Shortcomings of the Bohr Model

Bohr model of the hydrogen atom was no doubt an improvement over Rutherford nuclear model as it could account for the stability and the line spectra of the hydrogen atom. However, Bohr model could not explain the spectra of atoms containing more than one electron. It failed even for the simple helium atom which has only two electrons. Bohr model is adequate for hydrogen atom and hydrogen like systems such as He^+, Li^{2+} etc. Even for hydrogen atom, Bohr theory could not account for the fine structure in the spectrum observed using refined spectroscopic techniques. It is found that each spectral line on high resolution is in fact a doublet i.e. two closely spaced lines. Bohr's theory was also unable to account for the splitting of the spectral lines in the presence of a magnetic field (Zeeman effect) or an electric field (Stark effect).

3.4 TOWARDS QUANTUM MECHANICAL MODEL OF THE ATOM

In view of the shortcomings of the Bohr model, attempts were made to develop a more suitable and general model for atoms. Two important

Louis de Broglie (1892–1987)

De Broglie, a French physicist, studied history as an undergraduate in the early 1910's. His interest turned to science as a result of his assignment to radio communications in World War I. He received his Dr. Sc. from the University of Paris in 1924. He was professor of theoretical physics at the University of Paris from 1932 until his retirement in 1962. He was awarded the Nobel Prize in Physics in 1929.

developments which contributed significantly in the formulation of such a model were:

(i) Dual behaviour of matter, and

(ii) Heisenberg uncertainty principle

3.4.1 Dual Behaviour of Matter

The French physicist, Louis de Broglie in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wave- like properties. This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength. de Broglie, from this analogy, gave the following relation between wavelength (λ) and momentum (p), of a material particle.

$$\lambda = \frac{h}{mv} = \frac{h}{p} \qquad (3.15)$$

where m is the mass of the particle, v its velocity and p its momentum. de Broglie's prediction was confirmed experimentally when it was found that an electron beam undergoes diffraction, a phenomenon characteristic of waves. This fact has been put to use in making an electron microscope, which is based on the wave-like behaviour of electrons just as an ordinary microscope utilises the wave nature of light. An electron microscope is a powerful tool in modern scientific research because it achieves a magnification of about 15 million times.

It needs to be noted that according to de Broglie, every object in motion has a wave character. The wavelengths associated with ordinary objects are so short (because of their large mass) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can however be detected experimentally.

Example 3.10

What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 $m\ s^{-1}$?

Solution

According to de Broglie equation 3.15

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34}\ J\ s)}{(0.1\ kg)\ (10\ m\ s^{-1})}$$

$$= 6.626 \times 10^{-34}\ m\ [J = kg\ m^2\ s^{-2}]$$

Example 3.11

The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wave length.

Solution

Since K . E. = ½ mv^2

$$v = \left(\frac{2K.E.}{m}\right)^{1/2} = \left(\frac{2 \times 3.0 \times 10^{-25}\ kg\ m^2\ s^{-2}}{9.1 \times 10^{-31}\ kg}\right)^{1/2}$$

$$= 812\ m\ s^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ J\ s}{(9.1 \times 10^{-31}\ kg)\ (812\ m\ s^{-1})}$$

$$= 8967 \times 10^{-10}\ m = 8967\ Å$$

Example 3.12

Calculate the mass of a photon with wave length 3.6 Å.

Solution

$\lambda = 3.6\ \text{Å} = 3.6 \times 10^{-10}\ \text{m}$

velocity of photon = velocity of light.

$$m = \frac{h}{\lambda v} = \frac{6.626 \times 10^{-34}\ \text{J s}}{\left(3.6 \times 10^{-10}\ \text{m}\right)\left(3.0 \times 10^{8}\ \text{m s}^{-1}\right)}$$

$$= 6.135 \times 10^{-33}\ \text{kg}$$

3.4.2 Heisenberg Uncertainty Principle

Werner Heisenberg, a German physicist, in 1927 stated uncertainty principle which is the consequence of dual behaviour of matter and radiation. It states that **it is impossible to determine simultaneously the exact position and exact velocity of an electron**. This principle applies to all bodies but becomes significant when applied to bodies with small masses. Heisenberg was awarded the 1932 Nobel Prize in Physics.

The uncertainty principle can best be understood with the help of an example. Suppose you are asked to measure the thickness of a sheet of paper with an unmarked metrestick, obviously, the result obtained would be extremely inaccurate and meaningless. In order to obtain any accuracy, you would have to use an instrument graduated in units smaller than the thickness of a sheet of paper. Analogously, in order to determine the position of an electron, we must use a "metrestick" calibrated in units smaller than the dimensions of an electron. To observe an electron, we can illuminate it with "light" or electromagnetic radiation. The "light" used must have a wavelength smaller than the dimensions of an electron. But photon of such "light" would possess very high energy. The high momentum photons of such light $\left(p = \frac{h}{\lambda}\right)$ would change the energy of electrons by collision. In this process, we, no doubt, would be able to calculate the position of the electron, but we would know very little about the velocity of the electron after the collision.

Reasons for the Failure of the Bohr model

One can now understand the reasons for the failure of the Bohr model. In Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. The wave character of the electron is not considered in Bohr model. Further, an orbit is a clearly defined path and this path can completely be defined only if both the exact position and the exact velocity of the electron at the same time are known. This is not possible according to the Heisenberg uncertainty principle. *Bohr model of the hydrogen atom, therefore, not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle.* In view of these inherent weaknesses in the Bohr model, there was no point in extending Bohr model to other atoms. What was needed was an insight into the structure of the atom, which took into account wave-particle duality of matter and was consistent with Heisenberg uncertainty principle. This came with the advent of quantum mechanics.

3.5 QUANTUM MECHANICAL MODEL OF ATOM

Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone, orbiting planets etc., which have essentially a particle-like behaviour. However it fails when applied to microscopic objects like electrons, atoms, molecules etc. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter and the uncertainty principle. The branch of science that takes into account this dual behaviour of matter is called **quantum mechanics**.

Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties. It specifies the laws of motion that these objects obey. When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrödinger. Here, however, we shall be discussing the quantum mechanics of Schrödinger which is based on the ideas of wave motion. The fundamental equation of quantum mechanics is the **Schrödinger equation**. This was proposed by Schrödinger and it won him the Nobel Prize in Physics in 1933. This equation which incorporates wave-particle duality of

Erwin Schrödinger, an Austrian physicist received his Ph.D. in theoretical physics from the University of Vienna in 1910. In 1927 Schrödinger succeeded Max Planck at the University of Berlin at Planck's request. In 1933, Schrödinger left Berlin because of his opposition to Hitler and Nazi policies and returned to Austria in 1936. After the invasion of Austria by Germany, Schrödinger was forcibly removed from his professorship. He then moved to Dublin, Ireland where he remained for seventeen years. Schrödinger shared the Nobel Prize for Physics with P.A.M. Dirac in 1933.

Erwin Schrödinger (1887-1961)

matter as proposed by de Broglie is quite complex and we need knowledge of higher mathematics to solve it. We will learn its solutions for different systems in higher classes.

For a system (such as an atom or a molecule whose energy does not change with time) the Schrödinger equation is written as $\hat{H}\psi = E\psi$ where $\hat{H}$ is a mathematical operator called Hamiltonian. Schrödinger gave a recipe of constructing this operator from the expression for the total energy of the system. Solution of this equation gives E and ψ.

Hydrogen Atom and the Schrödinger Equation

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy states the electron can occupy and the corresponding wave function(s) (ψ) (also called **atomic orbitals** or hydrogen orbitals) of the electron associated with each energy state. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number m_l) arise as a natural consequence in the solution of the Schrödinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

Application of Schrödinger equation to multi-electron atoms presents a difficulty: the Schrödinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge– all the orbitals are somewhat contracted. Further, as you shall see later (in subsections 3.5.4 and 3.5.5), unlike hydrogen orbitals whose energies depend only on the quantum number n, the energies of the orbitals in multi-electron atoms depend on quantum numbers n and l.

3.5.1 Important Features of the Quantum Mechanical Model of Atom

Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrödinger equation to atoms. The following are the important features of the quantum-mechanical model of atom:

1. The energy of electrons in atoms is quantized (i.e., can only have certain specific values).
2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons.
3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom can, therefore, be never determined or known. That is why, as you shall see later on, one talks of the concept of probability of finding the electron at different points in an atom.
4. **An atomic orbital is the wave function ψ**

for an electron in an atom. Whenever an electron is described by a wave function, we say that the electron occupies that orbital. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. These one electron orbital wave functions or orbitals form the basis of the electronic structure of atoms. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For each electron of a multi-electron atom, there shall, therefore, be an orbital wave function characteristic of the orbital it occupies. All the information about the electron in an atom is stored in its orbital wave function ψ and quantum mechanics makes it possible to extract this information out of ψ.

5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as **probability density** and is always positive. ***From the value of $|\psi|^2$ at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.***

3.5.2 Orbitals and Quantum Numbers

A large number of orbitals are possible in an atom. Qualitatively these orbitals can be distinguished by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly shape and orientation mean that there is more probability of finding the electron along certain directions than along others.

Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labelled as n, l and m_l. **The principal quantum number, n,** is a positive integer with values of 1,2,3.....etc. The principal quantum number determines the size and to a large extent the energy of the orbital. For hydrogen and hydrogen-like systems (e.g. He^+, Li^{2+}), it alone determines the energy and size of the orbital. The larger the value of n, the larger is the energy of the orbital. The principal quantum number also identifies the shell. **There are n^2 orbitals in a shell. All the orbitals of a given value of n constitute a single shell of atom** and are represented by the following letters.

n	=	1	2	3	4
Shell	=	K	L	M	N

Each shell consists of one or more subshells or sublevels. The number of subshells in a

Orbit and orbital

Orbit and orbital are not synonymous. An orbit, as proposed by Bohr, is a circular path around the nucleus in which an electron moves. A precise description of this path of the electron is impossible according to Heisenberg uncertainty principle. Bohr orbits, therefore, have no real meaning and their existence can never be demonstrated experimentally. An atomic orbital, on the other hand, is a quantum mechanical concept and refers to the one electron wave function ψ in an atom. It is characterized by three quantum numbers (n, l and m_l) and its value depends upon the coordinates of the electron. ψ has, by itself, no physical meaning. It is the square of the wave function i.e., $|\psi|^2$ which has a physical meaning. $|\psi|^2$ at any point in an atom gives the value of probability density at that point. Probability density ($|\psi|^2$) is the probability per unit volume and the product of $|\psi|^2$ and a small volume (called a volume element) yields the probability of finding the electron in that volume (the reason for specifying a small volume element is that $|\psi|^2$ varies from one region to another in space but its value can be assumed to be constant within a small volume element). The total probability of finding the electron in a given volume can then be calculated by the sum of all the products of $|\psi|^2$ and the corresponding volume elements. It is thus possible to get the probable distribution of an electron in an orbital.

principal shell is equal to the value of n. There is only one subshell in the $n=1$ shell. There are two subshells in the $n=2$ shell, three in the $n=3$ shell, and so on. Each subshell in a shell is assigned an **azimuthal or subsidiary quantum number**, l.

For a given value of n, l can have n values ranging from 0 to $(n-1)$. For example, when n = 1, the only value of l is 0 and there is only one sub-shell. When n = 2, there are two subshells that have l values of 0 and 1, respectively. When n = 3, the three subshells have l values of 0, 1 and 2.

Subshells corresponding to different values of l are represented by the following symbols:

l	=	0,	1,	2,	3,	4,	5
notation		*s*,	*p*,	*d*,	*f*,	*g*,	*h*

Table 3.4 shows the permissible values of l for a given principal quantum number and the corresponding subshell notations.

Table 3.4 Subshell Notations

n	l	Subshell notation
1	0	1*s*
2	0	2*s*
2	1	2*p*
3	0	3*s*
3	1	3*p*
3	2	3*d*
4	0	4*s*
4	1	4*p*
4	2	4*d*
4	3	4*f*

Number of orbitals in a subshell

Each subshell consists of one or more orbitals. **The number of orbitals in a subshell is given by (2 l + 1)**. In any $l=0$ subshell, for example, there is 2(0) +1 = 1 orbital. In any $l=1$ subshell, there are 2(1) +1 = 3 orbitals. In any $l=2$ subshell, there are 2(2) + 1 = 5 orbitals. In other words,

Subshell notation	=	*s*,	*p*,	*d*,	*f*,	*g*
Value of l	=	0,	1,	2,	3,	4
Number of orbitals	=	1,	3,	5,	7,	9

An *s* subshell consists of one orbital, a *p* subshell consists of three orbitals, a *d* subshell consists of five orbitals and so on. The quantum number l also gives the shape of the orbitals in the subshell.

Each orbital within a given subshell is identified by a **magnetic orbital quantum number m_l** which gives information about the orientation of the orbital.

For any subshell (defined by l value) , $(2l+1)$ values of m_l are possible and these values are given by :

$$m_l = -l, -(l-1), \ldots 0, \ldots, (l-1), l$$

Thus, for $l=0$, the only permitted value of m_l is 0(one s orbital). For $l=1$, m_l can be -1,0 and +1 (three *p* orbitals). For $l=2$, m_l can be -2, -1, 0, +1 and +2 (five *d* orbitals). It should be noted that the values of m_l are derived from l and that the values of l are derived from n.

Each orbital in an atom, therefore, is identified by a set of values for n, l and m_l. An orbital described by the quantum numbers $n=2$, $l=1$ and $m_l=0$ is an orbital in the *p* subshell of the second shell- a 2*p* orbital.

The three quantum numbers labelling an atomic orbital can be used equally well to label the electron in the orbital. However, a fourth quantum number, the **spin quantum number m_s** is necessary to describe an electron completely. An electron has, besides charge and mass, intrinsic spin angular momentum commonly called spin. Spin angular momentum of the electron, a vector quantity, can have two orientations relative to a chosen axis. These two orientations are distinguished by the spin quantum number m_s which can take the values of + ½ or – ½. These are called the two ***spin states of the electron*** and are normally represented by the two arrows↑(spin up) and ↓(spin down) respectively. Two electrons that have different m_s values (one + ½ and the other – ½) are said to have opposite spins. An orbital cannot hold more than two electrons and these two electrons should have opposite spins.

To sum up, the four quantum numbers provide the following information:

1. n identifies the shell , determines the size of the orbital and and also to a large extent the energy of the orbital.
2. There are n subshells in the nth shell. l identifies the subshell and determines the

shape of the orbital. There are $(2l+1)$ orbitals of each type in a subshell i.e., one *s* orbital ($l = 0$), three p orbitals ($l = 1$) and five *d* orbitals ($l = 2$) per subshell. To some extent l also determines the energy of the orbital in a multi-electron atom.

3. m_l designates the orientation of the orbital. For a given value of l, m_l has $(2l+1)$ values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.
4. m_s refers to orientation of the spin of the electron.

Example 3.13

What is the total number of orbitals associated with the principal quantum number $n = 3$?

Solution

For $n = 3$, the possible values of l are 0, 1 and 2. Thus, there is one 3*s* orbital ($n = 3$, $l = 0$ and $m_l = 0$); there are three 3*p* orbitals ($n = 3$, $l = 1$ and $m_l = -1, 0, 1$) there are five 3*d* orbitals ($n=3$, $l=2$, $m_l = -2, -1, 0, 1, 2$)

Therefore, the total number of orbitals is 1+3+5=9.

Example 3.14

Using *s, p, d, f* notations, describe the orbital with the following quantum numbers (a) $n = 2$, $l=1$ (b) $n = 4$, $l = 0$ (c) $n = 5$, $l = 3$ (d) $n = 3$, $l = 2$.

Solution

	n	l	orbital
(a)	2	1	2*p*
(b)	4	0	4*s*
(c)	5	3	5*f*
(d)	3	2	3*d*

3.5.3 Shapes of Atomic Orbitals

The orbital wave function or orbital ψ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. The square of the wave function i.e. $|\psi|^2$, however, has a physical meaning. $|\psi|^2$ at a point in an atom is a measure of the probability density at that point. This interpretation of $|\psi|^2$ was given by German Physicist, Max Born. The probability density $|\psi|^2$ is not uniform in an atom; it is more in some regions and less in other regions. This, therefore, suggests that to interpret and visualize an atomic orbital, we should construct diagrams based on probability density $|\psi|^2$ values in an atom.

Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or a contour surface is drawn in space for an orbital on which the value of probability density $|\psi|^2$ is constant. In principle many such boundary surfaces for an orbital may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density* is taken to be a good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high say 90%. One may ask a question: Why don't we draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is 100%? The answer to this question is that the probability density $|\psi|^2$ has always some value, however small it may be, at any finite distance from the nucleus. It is, therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%.

Boundary surface diagram for 1*s* orbital is shown in Fig.3.8. This is actually a sphere centered on the nucleus. In two-dimensions, this sphere shall look like a circle. The boundary of the sphere encloses 90% probability of finding the electron. As already mentioned, for each

Fig.3.8 *Boundary surface diagram of the 1s orbital. For this orbital, both the wave function and the probability density have always positive signs.*

* *If probability density $|\psi|^2$ is constant on a given surface, $|\psi|$ is also constant over the surface. The boundary surfaces for $|\psi|^2$ and $|\psi|$ are identical.*

value of principal quantum number n, there is one s orbital. All s-orbitals are spherically symmetric i.e., the probability of finding the electron at a given distance is equal in all directions. The size of the s orbital increases with increase in n i.e., $4s>3s>2s>1s$.

Boundary surface diagrams for the three $2p$ orbitals (l =1) are shown in Fig.3.9. In these diagrams, the nucleus is at the origin. Here, unlike the s orbitals, the boundary surface diagrams are not spherical. Instead each p-orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The two lobes do not touch each other. The size, shape and energy of the three orbitals are identical. They differ, however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z-axis, they are given the designations $2p_x$, $2p_y$, and $2p_z$. It should be understood, however, that there is no simple relation between the values of m_l (-1,0 and +1) and the x, y, and z directions. For our purpose, it is sufficient to remember that, because there are three possible values of m_l, there are, therefore, three p orbitals whose axes are mutually perpendicular. Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is $4p>3p>2p$.

We shall study more about the shapes of the orbitals in the next class.

3.5.4 Energies of Orbitals

The energy of an electron in a hydrogen atom is determined solely by its principal quantum number. Thus, the energy of the orbitals increases as follows:

$1s<2s=2p<3s=3p=3d<4s=4p=4d=4f<.....$

Although the shapes of the $2s$ and $2p$ orbitals are different, an electron has the same energy when it is in the $2s$ orbital as when it is in the $2p$ orbital.

The $1s$ orbital in a hydrogen atom, as we have said, corresponds to the most stable condition and is called the ground state, and an electron residing in this orbital is most strongly held by the nucleus. An electron in the $2s$, $2p$, or higher orbitals in a hydrogen atom is in an excited state.

The energy of an electron in a many-electron atom, unlike that of the hydrogen atom, depends not only on its principal quantum number, but also on its azimuthal quantum number. The stability of an electron in a many-electron atom is the net result of the attraction between the electron and the nucleus and the repulsion between the electron and the rest of the electrons present. Both the attraction and the repulsion depend on the shell and the shape of the orbital in which the electron resides. Consequently, the order of increasing orbital energy for a many electron atom is more complicated and is usually determined by experiment. This order shall be discussed in the following section.

3.5.5 Filling of Orbitals in Atoms

The filling of electrons into the orbitals of different atoms takes place according to the Aufbau principle which is based on the Pauli's exclusion principle, the Hund's rule of maximum multiplicity and the relative energies of the orbitals.

Aufbau Principle. The word 'aufbau' in German

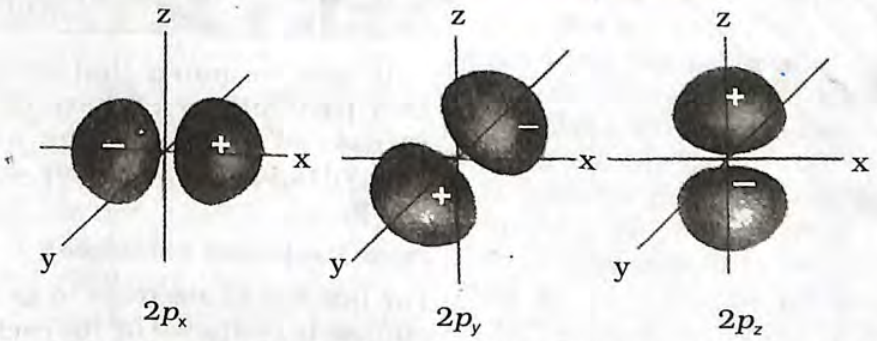

Fig.3.9 *Boundary surface diagrams of the three 2p orbitals. The indicated signs (positive and negative) are those of the corresponding wave functions and have no connection with positive or negative charge. These signs are indicated because they would be of interest later in discussion on the overlapping of orbitals in the context of chemical bonding in Unit-6. The probability density $|\psi|^2$ is, of course, always positive.*

means 'building up'. The building up of orbitals means the filling up of orbitals with electrons. The principle states:

In the ground state of the atoms, the orbitals are filled in order of their increasing energies. In other words, electrons first occupy the lowest-energy orbital available to them and enter into higher energy orbitals only when after the lower energy orbitals are filled.

The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows:

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*....

This order may be remembered by using the method given in Fig.3.10. Starting from the top, the direction of the arrows gives the order of filling of orbitals.

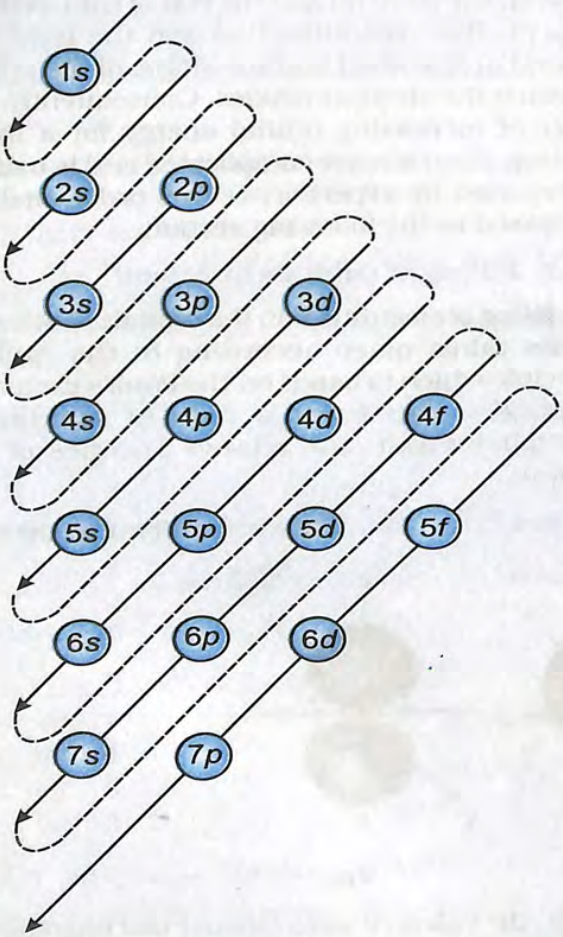

Fig.3.10 *Order of filling of orbitals*

Alternatively, the order of increase of energy of orbitals can be calculated from $(n+l)$ rule, explained below :

The lower the value of $(n+l)$ for an orbital, the lower is its energy. If two orbitals have the same $(n+l)$ value, the orbital with lower value of n has the lower energy.

The Table 3.5 illustates the $(n + l)$ rule :

Table 3.5 Arrangement of orbitals with increasing energy on the basis of $(n+l)$ rule

Orbital	Value of n	Value of l	Value of $(n + l)$	
1*s*	1	0	1 + 0 = 1	
2*s*	2	0	2 + 0 = 2	
2*p*	2	1	2 + 1 = 3	2*p* (n=2) has lower energy than 3*s*
3*s*	3	0	3 + 0 = 3	3*s* (n=3)
3*p*	3	1	3 + 1 = 4	3*p* (n =3) has lower energy than 4*s*
4*s*	4	0	4 + 0 = 4	4*s* (n =4)
3*d*	3	2	3 + 2 = 5	3*d* (n =3) has lower energy than 4*p*
4*p*	4	1	4 + 1 =5	4*p* (n =4)

It may be noted that different subshells of a particular shell have different energies in case of many-electron atoms. However in hydrogen atom, they have the same energy.

Pauli Exclusion Principle

The number of electrons to be filled in various orbitals is restricted by the exclusion principle, given by the Austrian scientist Wolfgang Pauli. According to this principle :

No two electrons in an atom can have the same set of four quantum numbers.

For example, if one electron in an atom has a particular set of four quantum numbers say n=1, l=0, $m_l = 0$ and $m_s = +½$, then all the other electrons in that atom are excluded from having this set of quantum numbers. This is the only exclusion, otherwise the electrons may assume all the states permitted by the combinations of quantum numbers.

Pauli was awarded the 1945 Nobel Prize in Physics.

Hund's Rule of Maximum Multiplicity

This rule deals with the filling of electrons into the orbitals belonging to the same subshell (i.e. orbitals of equal energy, called degenerate orbitals). It states: **pairing of electrons in the orbitals belonging to the same subshell (*p*, *d* or *f*) does not take place until each orbital belonging to that subshell has got one electron each, i.e., is singly occupied.**

Since there are three *p*, five *d* and seven *f* orbitals, therefore, the pairing of electrons will start in the *p*, *d* and *f* orbitals with the entry of 4th, 6th and 8th electron, respectively. It has been observed that half filled, and fully filled degenerate set of orbitals acquire extra stability due to their symmetry.

3.6 ELECTRONIC CONFIGURATIONS OF ATOMS

The distribution of electrons into orbitals of an atom is called its electronic configuration. If one keeps in mind the basic rules which govern the filling of different atomic orbitals, the electronic configurations of different atoms can be written very easily.

The hydrogen atom has only one electron which goes in the orbital with lowest energy, namely 1*s*. The electronic configuration of the hydrogen atom is $1s^1$ meaning it has one electron in the 1*s* orbital. The second electron in helium (He) can also occupy the 1s orbital. Its configuration is therefore, $1s^2$. The third electron of lithium (Li) is not allowed in the 1*s* orbital because of the Pauli principle. It therefore, takes the next available choice, namely the 2*s* orbital. The electronic configuration of lithium is $1s^2\ 2s^1$. The 2*s* orbital can accommodate one more electron. The configuration of the beryllium (Be) atom is, therefore, $1s^2\ 2s^2$ (see Table 3.6 for the electronic configurations of elements).

In the next six elements-boron (B, $1s^2,\ 2s^2,\ 2p^1$), carbon (C, $1s^2\ 2s^2\ 2p^2$), nitrogen (N, $1s^2\ 2s^2\ 2p^3$), oxygen (O, $1s^2\ 2s^2\ 2p^4$), fluorine (F, $1s^2\ 2s^2\ 2p^5$) and neon (Ne, $1s^2\ 2s^2\ 2p^6$) the 2*p* orbitals get progressively filled. This process is completed with the neon atom. The electronic configurations of the elements from sodium (Na, $1s^2\ 2s^2\ 2p^6\ 3s^1$) to argon (Ar, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$) follow exactly the same pattern as the elements from lithium to neon with the difference that the 3*s* and 3*p* orbitals are getting filled now. In potassium (K) and calcium (Ca), the 4*s* orbital, being lower in energy than the 3*d* orbitals, is occupied by one and two electrons respectively.

A new feature shows up beginning with scandium (Sc). The 3*d* orbital, being lower in energy than 4*p*, is filled first. Consequently, in the next ten elements, scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn)–the five 3*d* orbitals are progressively occupied. We may be puzzled by the fact that chromium and copper have five and ten electrons in 3*d* orbitals rather than four and nine as their position would have indicated (with one electron in the 4s orbital). The reason is that fully filled orbitals and half-filled orbitals have extra stability (i.e. lower energy). Thus the p^3, p^6, d^5, d^{10}, f^7, f^{14} etc. configurations, which are either fully filled or half-filled, are more stable. Chromium and copper therefore, adopt the d^5 and d^{10} configurations in preference to the d^4 and d^9 configurations.

With the saturation of the 3*d* orbitals, the filling of the 4*p* orbitals starts at gallium (Ga) and is complete at krypton (Kr). In the next eighteen elements from rubidum (Rb) to xenon (Xe), the pattern of filling the 5*s*, 4*d* and 5*p* orbitals is similar to that of 4*s*, 3*d* and 4*p* orbitals discussed above. Then comes the turn of the 6*s* orbital. In caesium (Cs) and barium (Ba), this orbital contains one and two electrons, respectively. Then from lanthanum (La) to mercury (Hg), the filling up of electrons takes place in 4*f* and 5*d* orbitals. After this, filling of 6*p*, then 7*s* and finally 5*f* and 6*d* orbitals takes place. The elements after uranium (U) are all short-lived and all of them are produced artificially.

One may ask what is the utility of knowing

the electron configuration? The modern approach to chemistry, in fact, depends almost entirely on electron distributions to understand and explain chemical behaviour. For example, questions like why two or more than two atoms combine to form molecules, why some elements are metals while others are non-metals, why elements like helium and argon are not reactive but elements like the halogens are reactive, find simple explanation from the electronic configuration. These questions have no answers in the Daltonian model of an atom. A detailed understanding of the electronic structure of atoms is, therefore, very essential for gaining an insight into the various aspects of modern chemical knowledge.

SUMMARY

Atoms are the building blocks of elements. They are the smallest parts of an element that chemically react like a bulk sample of the element. The first atomic theory, proposed by John Dalton in 1808, regarded atom as the ultimate indivisible particle of matter. Towards the end of the nineteenth century it was proved experimentally that atoms are divisible and consist of three fundamental particles: electrons, protons and neutrons. The discovery of sub-atomic particles led to the proposal of various atomic models to explain the structure of atom.

Thomson in 1898 proposed that an atom consists of uniform sphere of positive electricity with electrons embedded into it. This model in which mass of the atom is considered to be evenly spread over the atom was proved wrong by Rutherford's famous alpha-particle scattering experiment in 1909. Rutherford concluded that atom consists of a tiny positively charged nucleus, consisting of massive particles at its centre with electrons revolving around it in circular orbits. Rutherford model, which resembles the solar system, was no doubt an improvement over Thomson model but it could not account for the stability of the atom i.e., why does the electron not fall into the nucleus. Further it was also silent about the electronic structure of atoms i.e. about the distribution and relative energies of electrons around the nucleus. The difficulties of the Rutherford model were overcome by Niels Bohr in 1913 in his model of the hydrogen atom. Bohr postulated that electron moves around the nucleus in circular orbits. Only certain orbits can exist and each orbit corresponds to a specific energy. Bohr calculated the energy of electron in various orbits and for each orbit predicted the distance between the electron and nucleus. Bohr model, though offering a satisfactory model for explaining the spectra of the hydrogen atom, could not explain the spectra of multi-electron atoms. The reason for this was soon discovered. In Bohr model, an electron is regarded as a charged particle moving in a well defined circular orbit about the nucleus. The wave character of the electron is ignored in Bohr's theory. Further an orbit is a clearly defined path and this path can completely be defined only if both the exact position and the exact velocity of the electron at the same time are known. This is not possible according to the Heisenberg uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores the dual behaviour of electron but also contradicts Heisenberg uncertainty principle.

Erwin Schrödinger, in 1926, proposed an equation called Schrödinger equation to describe the electron distributions in space and the allowed energy levels in atoms. This equation incorporates de Broglie's concept of wave-particle duality and is consistent with Heisenberg uncertainty principle. When Schrödinger equation is solved for the electron in a hydrogen atom, the solution gives the possible energy states the electron can occupy and the corresponding wave function(s) (ψ) (which in fact are the mathematical functions) of the electron associated with each energy state. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number m_l) arise as a natural consequence in the solution of the Schrödinger equation. The restrictions on the values of these three quantum numbers also come naturally from this solution. The quantum mechanical model of the hydrogen atom successfully predicts all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

According to the quantum mechanical model of the atom, the electron distribution of an atom containing a number of electrons is divided into shells. The shells, in turn, are thought to consist of

one or more subshells and subshells are assumed to be composed of one or more orbitals, which the electrons occupy. While for hydrogen and hydrogen like systems (such as He^+, Li^{2+} etc.) all the orbitals within a given shell have same energy, the energy of the orbitals in a multi-electron atom depends upon the values of n and l: The lower the value of $(n + l)$ for an orbital, the lower is its energy. If two orbitals have the same $(n + l)$ value, the orbital with lower value of n has the lower energy. In an atom many such orbitals are possible and electrons are filled in those orbitals in order of increasing energy in accordance with Pauli exclusion principle (no two electrons in an atom can have the same set of four quantum numbers) and Hund's rule of maximum multiplicity (pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital belonging to that subshell has got one electron each, i.e., is singly occupied). This forms the basis of the electronic structure of atoms.

Table 3.6 Electronic Configurations of the Elements

Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	2	2	6	2	3													
S	16	2	2	6	2	4													
Cl	17	2	2	6	2	5													
Ar	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	2	6	2	6	3	2											
Cr*	24	2	2	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu*	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38	2	2	6	2	6	10	2	6			2							
Y	39	2	2	6	2	6	10	2	6	1		2							
Zr	40	2	2	6	2	6	10	2	6	2		2							
Nb*	41	2	2	6	2	6	10	2	6	4		1							
Mo*	42	2	2	6	2	6	10	2	6	5		1							
Tc	43	2	2	6	2	6	10	2	6	5		2							
Ru*	44	2	2	6	2	6	10	2	6	7		1							
Rh*	45	2	2	6	2	6	10	2	6	8		1							
Pd*	46	2	2	6	2	6	10	2	6	10									
Ag*	47	2	2	6	2	6	10	2	6	10		1							
Cd	48	2	2	6	2	6	10	2	6	10		2							
In	49	2	2	6	2	6	10	2	6	10		2	1						
Sn	50	2	2	6	2	6	10	2	6	10		2	2						
Sb	51	2	2	6	2	6	10	2	6	10		2	3						
Te	52	2	2	6	2	6	10	2	6	10		2	4						
I	53	2	2	6	2	6	10	2	6	10		2	5						
Xe	54	2	2	6	2	6	10	2	6	10		2	6						

* Elements with exceptional electronic configurations

Element	Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
Cs	55	2	2	6	2	6	10	2	6	10		2	6			1			
Ba	56	2	2	6	2	6	10	2	6	10		2	6			2			
La*	57	2	2	6	2	6	10	2	6	10		2	6	1		2			
Ce*	58	2	2	6	2	6	10	2	6	10	2	2	6			2			
Pr	59	2	2	6	2	6	10	2	6	10	3	2	6			2			
Nd	60	2	2	6	2	6	10	2	6	10	4	2	6			2			
Pm	61	2	2	6	2	6	10	2	6	10	5	2	6			2			
Sm	62	2	2	6	2	6	10	2	6	10	6	2	6			2			
Eu	63	2	2	6	2	6	10	2	6	10	7	2	6			2			
Gd*	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
Tb	65	2	2	6	2	6	10	2	6	10	9	2	6			2			
Dy	66	2	2	6	2	6	10	2	6	10	10	2	6			2			
Ho	67	2	2	6	2	6	10	2	6	10	11	2	6			2			
Er	68	2	2	6	2	6	10	2	6	10	12	2	6			2			
Tm	69	2	2	6	2	6	10	2	6	10	13	2	6			2			
Yb	70	2	2	6	2	6	10	2	6	10	14	2	6			2			
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
Pt*	78	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
Au*	79	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
Es	99	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
Md	101	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
No	102	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
Lr	103	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
Rf	104	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	2	2
Db	105	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	3	2
Sg	106	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	4	2
Bh	107	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	5	2
Hs	108	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	6	2
Mt**	109	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	7	2

* Elements with atomic number 110 and above have been reported but not yet fully authenticated and named.

EXERCISES

3.1 (i) Calculate the number of electrons which will together weigh one gram.
(ii) Calculate the mass and charge of one mole of electrons.

3.2 (i) Calculate the total number of electrons present in 1 mol of methane.
(ii) Find (a) the total number and (b) the total mass of neutrons in 7 mg of 14C. (Assume that mass of a neutron = 1.675×10^{-27} kg).
(iii) Find (a) the total number and (b) the total mass of protons in 34 mg of NH_3 at S.T.P.
Will the answer change if the temperature and pressure are changed ?

3.3 How many neutrons and protons are there in the following nuclei :
$^{13}_{6}C$, $^{16}_{8}O$, $^{24}_{12}Mg$, $^{56}_{26}Fe$, $^{88}_{38}Sr$

3.4 Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A)
(i) Z = 17 , A = 35.
(ii) Z = 92 , A = 233.
(iii) Z = 4 , A = 9.

3.5 Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (ν) and wave number $\bar{\nu}$ of the yellow light.

3.6 Find energy of each of the photons which
(i) correspond to light of frequency 3×10^{15} Hz.
(ii) have wavelength of 0.50 Å.

3.7 Calculate the wavelength, frequency and wave number of a light wave whose period is 2.0×10^{-10} s.

3.8 What is the number of photons of light with a wavelength of 4000 pm that provide 1J of energy?

3.9 A photon of wavelength 4×10^{-7} m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate (i) the energy of the photon (eV) (ii) the kinetic energy of the emission and (iii) the velocity of the photoelectron (1 eV= 1.6020×10^{-19}J).

3.10 Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

3.11 A 25 watt bulb emits monochromatic yellow light of wavelength of 0.57μm. Calculate the rate of emission of quanta per second.

3.12 Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (ν_0) and work function (W_0) of the metal.

3.13 What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with n = 4 to an energy level with n = 2?

3.14 How much energy is required to ionise a H atom if the electron occupies n = 5 orbit? Compare your answer with the ionization energy of H atom (energy required to remove the electron from n =1 orbit).

3.15 What is the maximum number of emission lines when the excited electron of a H atom in n = 6 drops to the ground state?

3.16 (i) The energy associated with the first orbit in the hydrogen atom is -2.18×10^{-18} J $atom^{-1}$. What is the energy associated with the fifth orbit?
(ii) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

3.17 Calculate the wave number for the longest wavelength transition in the Balmer series of atomic hydrogen.

3.18 What is the energy in joules, required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state? The ground state electron energy is -2.18×10^{-11} ergs.

3.19 The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2$ J. Calculate the energy required to remove an electron completely from the n = 2 orbit. What is the longest wavelength of light in cm that can be used to cause this transition?

3.20 Calculate the wavelength of an electron moving with a velocity of 2.05×10^7 m s^{-1}.

3.21 The mass of an electron is 9.1×10^{-31} kg. If its K.E. is 3.0×10^{-25} J, calculate its wave length.

3.22 Which of the following are isoelectronic species, i.e. those having the same number of electrons?

Na^+, K^+, Mg^{2+}, Ca^{2+}, S^{2-}, Ar.

3.23 (i) Write the electronic configurations of the following ions: (a) H^-; (b) Na^+; (c) O^{2-} (d) F^-

(ii) What are the atomic numbers of elements whose outermost electrons are represented by (a) $3s^1$; (b) $2p^3$ and (c) $3d^6$?

(iii) What atoms are indicated by the following configurations ?
(a) [He] $2s^1$; (b) [Ne] $3s^2\ 3p^3$; (c) [Ar] $4s^2\ 3d^1$.

3.24 What is the lowest value of n that allows g orbitals to exist?

3.25 An electron is in one of the 3*d* orbitals. Give the possible values of *n*, ℓ and m_l for this electron.

3.26 An atom of an element contains 29 electrons and 35 neutrons. Deduce (i) the number of protons and (ii) the electronic configuration of the element.

3.27 Give the number of electrons in the species H_2^+, H_2 and O_2^+

3.28 (i) An atomic orbital has $n = 3$. What are the possible values of l and m_l ?
(ii) List the quantum numbers (m_l and l) of electrons for 3*d* orbital.
(iii) Which of the following orbitals are possible?
1*p*, 2*s*, 2*p* and 3*f*

3.29 Using *s*, *p*, *d* notations, describe the orbital with the following quantum numbers.
(a) n=1, l=0; (b) $n = 3$; l=1 (c) $n = 4$; $l = 2$; (d) n=4; l=3.

3.30 Explain, giving reasons, which of the following sets of quantum numbers are not possible.

(a) $n = 0$, $l = 0$, $m_l = 0$, $m_s = +\frac{1}{2}$
(b) $n = 1$, $l = 0$, $m_l = 0$, $m_s = -\frac{1}{2}$
(c) $n = 1$, $l = 1$, $m_l = -0$, $m_s = +\frac{1}{2}$
(d) $n = 2$, $l = 1$, $m_l = 0$, $m_s = -\frac{1}{2}$
(e) $n = 3$, $l = 3$, $m_l = -3$, $m_s = +\frac{1}{2}$
(f) $n = 3$, $l = 1$, $m_l = 0$, $m_s = +\frac{1}{2}$

3.31 How many electrons in an atom may have the following quantum numbers?
(a) $n = 4$, $m_s = -\frac{1}{2}$ (b) $n = 3$, $l = 0$

3.32 Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit.

3.33 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum ?

3.34 Calculate the energy required for the process

$He^+(g) \rightarrow He^{2+}(g) + e^-$

The ionization energy for the H atom in the ground state is 2.18×10^{-18} J $atom^{-1}$

UNIT 4

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Objectives

After studying this Unit, you will be able to

- know the historical development of Periodic Table.
- understand the periodic law and the electronic configuration of atoms as the basis for periodic classification.
- know IUPAC nomenclature for elements with Z > 100.
- Classify elements into s, p, *d*, *f* blocks and learn their main characteristics.
- recognize the periodicity in physical and chemical properties of elements.

"The Periodic Table of elements is one of the most powerful icons in Science : a single document that consolidates much of our knowledge of chemistry"

The Periodic Table of elements is an important landmark in the history of chemistry. It is considered as one of the great scientific achievements. It is difficult to study individually the chemistry of more than one hundred elements known today and their innumerable compounds. The Periodic Table provides a systematic and extremely useful framework for organizing the vast amount of information available on the chemical behaviour of the elements into a few simple and logical patterns. The elements are arranged in rows and columns. Knowing the position of an element in the Periodic Table, it is possible to predict its chemistry. In this Unit, we will study the historical development of the Periodic Table as it stands today and the statement of modern Periodic Law. We will also learn how the periodic classification follows as a logical consequence of the electronic configuration of atoms. Finally we will examine some of the periodic trends in the physical and chemical properties of the elements.

4.1 GENESIS OF PERIODIC CLASSIFICATION : FROM DOEBEREINER TO MENDELEEV

Several chemists have for long tried to classify the elements and to find patterns in their properties. The German chemist, John Doebereiner in 1817 pointed out that there were sets of three elements (**Triads**) which showed similar chemical properties. He also noted the fact that the atomic weight of the central element of the **Triad** was approximately the mean of the atomic weights of the other two members. (see Table 4.1) and the properties of the middle element were in between those of the end members. The English chemist John Newlands, in 1865-66, developed the **Law of Octaves**. He arranged the elements in increasing order of their atomic weights and noted

that any given element was similar to the eighth element that followed it. The relationship was the same as that existing between a musical note and its octave. At that time, this idea was not widely accepted and was viewed with disbelief and even ridiculed. His work was recognized much later by the Royal Society, London by awarding him the Davy Medal in 1887.

A breakthrough in the development of the Periodic Table came with the work of the Russian Chemist Dmitri I. Mendeleev (1834-1907) and the German Chemist J. Lothar Meyer (1830-1895). Working independently, both the scientists in 1869 proposed that when the elements are arranged in the increasing order of their atomic weights, similarities in physical and chemical properties appear at regular intervals. The results published by both were very similar. Lother Meyer used the physical properties such as atomic volume, melting point and boiling point to construct a plot showing similarities among particular sets of elements. Mendeleev's system was more elaborate. He used a broader range of physical and chemical properties to classify the elements. In particular, Mendeleev relied on the similarities in the empirical formulae and properties of the compounds formed by the elements. Mendeleev stated his Periodic Law as:

The properties of the elements are a periodic function of their atomic weights.

Mendeleev is usually given the credit for the design of the Periodic Table as we know it today. He was certainly the first to fully recognize the significance of periodicity. He realized that some of the elements did not fit in with his scheme of classification if the order of the atomic weights was strictly followed. Placing full faith in the Periodic Law, Mendeleev was convinced that some of the atomic weight measurements were wrong.

Table 4.1 Doebereiner's Triads

Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

He ignored the order of the atomic weights to place together elements which had similar chemical properties. He also had the courage and foresight to leave gaps in the table for elements which were not known at that time. He predicted the properties of those missing elements from the known properties of the other elements in the same group. For example, gallium and germanium were not discovered at the time Mendeleev published his Periodic Table. He named these elements **Eka-Aluminium** and **Eka-Silicon**. These elements were discovered later and Mendeleev's foresight and intuition were vindicated. Some of the properties predicted by Mendeleev for these elements and those found experimentally are listed in Table 4.2. Fig.4.1 shows Mendeleev's Periodic Table published in 1905.

We must remember that when Mendeleev published his Periodic Table, no one had any idea of the structure of an atom. Several decades

Table 4.2 Mendeleev's Predictions for the Elements Eka-aluminium (Gallium) and Eka-silicon (Germanium)

Property	eka-aluminium (predicted)	gallium (found)	eka-silicon (predicted)	germanium (found)
Atomic Mass	68	70	72	72.6
Density /(g/cm^3)	5.9	5.94	5.5	5.36
Melting point (K)	Low	30.2	High	1231
Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Formula of chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$

Dmitri Ivanovich Mendeleev (1834-1907)

Dmitri Mendeleev, the youngest of a family of seventeen children was born in Tobalsk, Siberia in Russia. After his father's death, the family moved to St. Petersburg. He received his Master's degree in Chemistry in 1856 and the doctoral degree in 1865. He taught at the University of St.Petersburg where he was appointed Professor of General Chemistry in 1867. Preliminary work for his great textbook "Principles of Chemistry" led Mendeleev to propose the ***Periodic Law*** *and to construct his* ***Periodic Table*** *of elements. At that time, the structure of atom was unknown and Mendeleev's idea to consider that the properties of the elements were in someway related to their atomic masses was a very imaginative one. To place certain elements into the correct group from the point of view of their chemical properties, Mendeleev reversed the order of some pairs of elements and asserted that their atomic masses were incorrect. Mendeleev also had the foresight to leave gaps in the Periodic Table for elements unknown at that time and predict their properties from the trends that he observed among the properties of related elements. Mendeleev's predictions were proved to be astonishingly correct when these elements were discovered later.*

Mendeleev's Periodic Law spurred several areas of research during the subsequent decades. The discovery of the first two noble gases helium and argon in 1890 suggested the possibility that there must be other similar elements to fill an entire family. This idea led Ramsay to his successful search for krypton and xenon. Work on the radioactive decay series for uranium and thorium in the early years of twentieth century was also guided by the Periodic Table.

Mendeleev was a versatile genius who was interested in many fields of science. He worked on many problems connected with Russia's natural resources. He invented an accurate barometer. In 1890, he resigned his Professorship. He was appointed as the Director of the Bureau of Weights and Measures. He continued to carry out important research work in many areas until his death in 1907.

You will notice from the modern Period Table (Fig. 4.2) that Mendeleev's name has been immortalized by naming the element with atomic number 101, as Mendeleevium. This name was proposed by American scientist Glenn T. Seaborg, the discoverer of this element, "in recognition of the pioneering role of the great Russian Chemist who was the first to use the periodic system of elements to predict the chemical properties of undiscovered elements, a principle which has been the key to the discovery of nearly all the transuranium elements".

SERIES	GROUPS OF ELEMENTS								
	0	I	II	III	IV	V	VI	VII	VIII
1	-	Hydrogen H 1.008	-	-					
2	Helium He 4.0	Lithium Li 7.03	Beryllium Be 9.1	Boron B 11.0	Carbon C 12.0	Nitrogen N 14.04	Oxygen O 16.00	Fluorine F 19.0	
3	Neon Ne 19.9	Sodium Na 23.5	Magnesium Mg 24.3	Aluminium Al 27.0	Silicon Si 28.4	Phosphorus P 31.0	Sulphur S 32.06	Chlorine Cl 35.45	
4	Argon Ar 38	Potassium K 39.1	Calcium Ca 40.1	Scandium Sc 44.1	Titanium Ti 48.1	Vanadium V 51.4	Chromium Cr 52.1	Manganese Mn 55.0	Iron Fe 55.9 / Cobalt Co 59 / Nickel Ni 59 / (Cu)
5		Copper Cu 63.6	Zinc Zn 65.4	Gallium Ga 70.0	Germanium Ge 72.3	Arsenic As 75	Selenium Se 79	Bromine Br 79.95	
6	Krypton Kr 81.8	Rubidium Rb 85.4	Stronium Sr 87.6	Yttrium Y 89.0	Zirconium Zr 90.6	Niobium Nb 94.0	Molybdenum Mo 96.0	-	Ruthenium Ru 101.7 / Rhodium Rh 103.0 / Palladium Pd 106.5 / (Ag)
7		Silver Ag 107.9	Cadmium Cd 112.4	Indium In 114.0	Tin Sn 119.0	Antimony Sb 120.0	Tellurium Te 127	Iodine I 127	
8	Xenon Xe 128	Caesium Cs 132.9	Barium Ba 137.4	Lanthanum La 139	Cerium Ce 140	-	-	-	
9		-	-	-	-	-	-	-	
10	-	-	-	Ytterbium Yb 173	-	Tantalum Ta 183	Tungsten W 184	-	Osmium Os 191 / Iridium Ir 193 / Platinum Pt 194.9 / (Au)
11		Gold Au 197.2	Mercury Hg 200.0	Thallium Tl 204.1	Lead Pb 206.9	Bismuth Bi 208	-	-	
12	-	-	Radium Ra 224	-	Thorium Th 232	-	Uranium U 239		
	R	R_2O	RO	R_2O_3	HIGHER SALINE OXIDES RO_2		R_2O_5 RO_3	R_2O_7	RO_4
					HIGHER GASEOUS HYDROGEN COMPOUNDS RH_4		RH_3 RH_2	RH	

Fig. 4.1. Mendeleev's Periodic Table published in 1905

had to pass before the electron was discovered and the modern theory of atomic structure developed (Unit 3). In the next Section, we will see how atomic number and electronic configuration provided a fundamental basis for the periodic classification of elements.

4.2 MODERN PERIODIC LAW AND THE PRESENT FORM OF THE PERIODIC TABLE

As we saw in the last Section, Mendeleev's classification of elements was based on their atomic weights and several anomalies persisted in the Table with regard to the correct order of atomic weights (potassium and argon; cobalt and nickel, tellurium and iodine). The empirical evolution of the Periodic Table reached its peak in 1913, when the English Physicist Mosley showed that the **atomic number** is a more fundamental property of an element than its atomic mass. The position of an element in the Periodic Table depends on its atomic number and the reason for the anomalies in the Mendeleev's Periodic Table at once becomes clear. The Mendeleev Periodic Law was then modified as follows.

The physical and chemical properties of the elements are periodic functions of their atomic numbers.

You may recall that the atomic number is equal to the nuclear charge (the number of protons) or the number of electrons in a neutral atom. The original form of the periodic table has since been extensively modified as a result of the discovery of noble gases and the elucidation of the structure of atom. Furthermore it is now recognized that the periodic law is essentially the consequence of the periodic variation in electronic configurations, which indeed determine the physical and chemical properties of the elements and their compounds.

Numerous forms of the Periodic Table have been devised from time to time. A modern version, which is most convenient and widely used, is shown in Fig. 4.2. The horizontal rows (which Mendeleev called series) are called **Periods**. Elements having similar outer electronic configurations in their atoms are grouped in vertical columns; these are referred to as **Groups** or **Families**. According to the recommendation of IUPAC (International Union of Pure and Applied Chemistry), the groups are numbered from 1 to 18 replacing the older notation of groups 0, IA, IIA ..... VIIA, VIII, IB..... VIIB. There are altogether seven periods, three short and four long ones. The first period contains 2 elements. The subsequent periods consist of 8, 8, 18, 18 and 32 elements respectively. The seventh period is incomplete and like the sixth period would have a theoretical maximum of 32 elements.

4.3 NOMENCLATURE OF THE ELEMENTS WITH ATOMIC NO. > 100

The naming of the new elements had been left earlier traditionally to its discoverer (or discoverers) and the suggested name was ratified by the IUPAC. In recent years, disputes have arisen over the original discoveries of some of the elements of atomic number 104 and above. After several years of protracted discussion by the Commission on Nomenclature of Inorganic Chemistry (CNIC) appointed by IUPAC in 1994 and after eliciting comments from chemists around the world, IUPAC in 1997 finally came up with the approved official names for elements with atomic numbers 104 to 109. These are shown in Table 4.3. The names for elements with atomic numbers 110 and beyond have yet to be officially announced. However IUPAC has recommended a nomenclature to be followed for naming these new elements until their names are officially recognized. This nomenclature is based on the Latin words for the atomic number of the elements. The names are derived directly from the atomic number using the numerical roots for 0 and numbers 1-9. These are shown in Table 4.4. The roots are strung together in the order of digits which makes up the atomic number and "ium" is added at the end. The IUPAC names for elements with Z above 103 are shown in Table 4.3. As of now, elements with atomic numbers upto 112 and 114 have been discovered. Elements with Z = 113, 115 and beyond are not known

Example 4.1

What would be the IUPAC name and symbol for the element with atomic number 120 ?

Solution

From Table 4 .4, the roots for 1,2 and 0 are un, bi and nil respectively. Hence the name and the symbol respectively are unbinilium and Ubn.

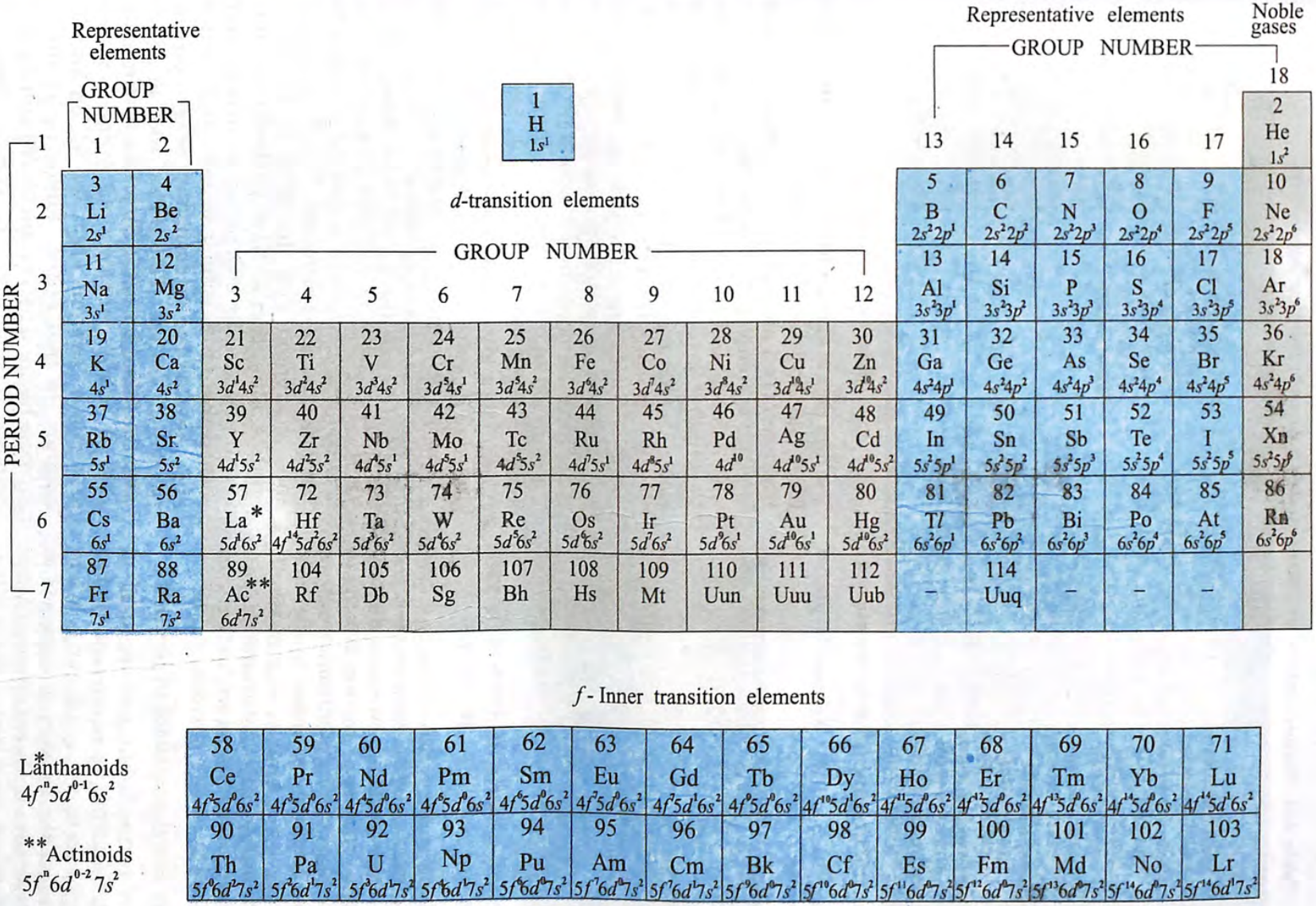
Representative elements
GROUP NUMBER
1 2
Representative elements
GROUP NUMBER
13 14 15 16 17
Noble gases
18
1 H $1s^1$
2 He $1s^2$
PERIOD NUMBER
1
2 Li $2s^1$ Be $2s^2$ B $2s^2 2p^1$ C $2s^2 2p^2$ N $2s^2 2p^3$ O $2s^2 2p^4$ F $2s^2 2p^5$ Ne $2s^2 2p^6$
3 Na $3s^1$ Mg $3s^2$ Al $3s^2 3p^1$ Si $3s^2 3p^2$ P $3s^2 3p^3$ S $3s^2 3p^4$ Cl $3s^2 3p^5$ Ar $3s^2 3p^6$
d-transition elements
GROUP NUMBER
3 4 5 6 7 8 9 10 11 12
4 K $4s^1$ Ca $4s^2$ Sc $3d^1 4s^2$ Ti $3d^2 4s^2$ V $3d^3 4s^2$ Cr $3d^5 4s^1$ Mn $3d^5 4s^2$ Fe $3d^6 4s^2$ Co $3d^7 4s^2$ Ni $3d^8 4s^2$ Cu $3d^{10} 4s^1$ Zn $3d^{10} 4s^2$ Ga $4s^2 4p^1$ Ge $4s^2 4p^2$ As $4s^2 4p^3$ Se $4s^2 4p^4$ Br $4s^2 4p^5$ Kr $4s^2 4p^6$
5 Rb $5s^1$ Sr $5s^2$ Y $4d^1 5s^2$ Zr $4d^2 5s^2$ Nb $4d^4 5s^1$ Mo $4d^5 5s^1$ Tc $4d^5 5s^2$ Ru $4d^7 5s^1$ Rh $4d^8 5s^1$ Pd $4d^{10}$ Ag $4d^{10} 5s^1$ Cd $4d^{10} 5s^2$ In $5s^2 5p^1$ Sn $5s^2 5p^2$ Sb $5s^2 5p^3$ Te $5s^2 5p^4$ I $5s^2 5p^5$ Xn $5s^2 5p^6$
6 Cs $6s^1$ Ba $6s^2$ 57 La* $5d^1 6s^2$ Hf $4f^{14} 5d^2 6s^2$ Ta $5d^3 6s^2$ W $5d^4 6s^2$ Re $5d^5 6s^2$ Os $5d^6 6s^2$ Ir $5d^7 6s^2$ Pt $5d^9 6s^1$ Au $5d^{10} 6s^1$ Hg $5d^{10} 6s^2$ Tl $6s^2 6p^1$ Pb $6s^2 6p^2$ Bi $6s^2 6p^3$ Po $6s^2 6p^4$ At $6s^2 6p^5$ Rn $6s^2 6p^6$
7 Fr $7s^1$ Ra $7s^2$ 89 Ac** $6d^1 7s^2$ 104 Rf Db 105 Sg 106 Bh 107 Hs 108 Mt 109 Uun 110 Uuu 111 Uub 112 – 114 Uuq – – –
f- Inner transition elements
*Lanthanoids $4f^n 5d^{0-1} 6s^2$
58 Ce $4f^2 5d^0 6s^2$ 59 Pr $4f^3 5d^0 6s^2$ 60 Nd $4f^4 5d^0 6s^2$ 61 Pm $4f^5 5d^0 6s^2$ 62 Sm $4f^6 5d^0 6s^2$ 63 Eu $4f^7 5d^0 6s^2$ 64 Gd $4f^7 5d^1 6s^2$ 65 Tb $4f^9 5d^0 6s^2$ 66 Dy $4f^{10} 5d^1 6s^2$ 67 Ho $4f^{11} 5d^0 6s^2$ 68 Er $4f^{12} 5d^0 6s^2$ 69 Tm $4f^{13} 5d^0 6s^2$ 70 Yb $4f^{14} 5d^0 6s^2$ 71 Lu $4f^{14} 5d^1 6s^2$
**Actinoids $5f^n 6d^{0-2} 7s^2$
90 Th $5f^0 6d^2 7s^2$ 91 Pa $5f^2 6d^1 7s^2$ 92 U $5f^3 6d^1 7s^2$ 93 Np $5f^4 6d^1 7s^2$ 94 Pu $5f^6 6d^0 7s^2$ 95 Am $5f^7 6d^0 7s^2$ 96 Cm $5f^7 6d^1 7s^2$ 97 Bk $5f^9 6d^0 7s^2$ 98 Cf $5f^{10} 6d^0 7s^2$ 99 Es $5f^{11} 6d^0 7s^2$ 100 Fm $5f^{12} 6d^0 7s^2$ 101 Md $5f^{13} 6d^0 7s^2$ 102 No $5f^{14} 6d^0 7s^2$ 103 Lr $5f^{14} 6d^1 7s^2$

Fig. 4.2 *Long form of the Periodic Table of the Elements with their atomic numbers and ground state outer electronic configurations. The groups are numbered 1-18 in accord with the 1984 IUPAC recommendations. This notation replaces the old numbering scheme of IA-VIIA , IB-VIIB and VIII for s-, p-, and d-block elements.*

Table 4.3 Nomenclature of Elements with Atomic Number Above 103

Atomic number	Name	Symbol	IUPAC Official Name	IUPAC Symbol
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassnium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnillium	Uun	*	*
111	Unununnium	Uuu	*	*
112	Ununbium	Uub	*	*
113	Ununtrium	Uut	+	
114	Ununquadium	Uuq	*	*
115	Ununpentium	Uup	+	
116	Ununhexium	Uuh	+	
117	Ununseptium	Uus	+	
118	Ununoctium	Uuo	+	

* *Official IUPAC name yet to be announced* + *Elements yet to be discovered*

Table 4.4 Notation for IUPAC Nomenclature of Elements

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

4.4 ELECTRONIC CONFIGURATIONS OF THE ELEMENTS AND PERIODIC TABLE

There is a close connection between the electronic configurations of the elements and the long form of the Periodic Table. We have already learnt that an electron in an atom is characterized by a set of four quantum numbers and the principal quantum number (n) defines the main energy level known as the **Shell**. The electronic configuration of elements can be best studied in terms of variations in periods and groups of the periodic table.

(a) Electronic Configurations in periods

Each successive period in the periodic table is associated with the filling up of the next higher principal energy level (n = 1, n = 2, etc.). It can be readily seen that the number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled.

The first period starts with the filling of the lowest level (1s) and has thus the two elements – hydrogen ($1s^1$) and helium ($1s^2$) when the first shell (K) is completed. The second period starts with lithium and the third electron enters the $2s$ orbital. The next element, beryllium has four electrons and has the electronic configuration $1s^2 2s^2$. Starting from the next element boron, the $2p$ orbitals are filled with electrons when the L shell is completed at neon ($2s^2\ 2p^6$). Thus there are 8 elements in the second period. The third period (n = 3) begins at sodium, and the added electron enters a $3s$ orbital. Successive filling of $3s$ and $3p$ orbitals gives rise to the third period of 8 elements from sodium to argon.

The fourth period (n=4) starts at potassium with the filling up of $4s$ orbital. Now you may note that before the $4p$ orbital is filled, filling up of $3d$ orbitals becomes energetically favourable and we come across the so called $3d$ Transition Series of elements. The fourth period ends at krypton with the filling up of the $4p$ orbitals. Altogether we have 18 elements in this fourth period. The fifth period (n=5) beginning with rubidium is similar to the fourth period and contains the $4d$ transition series starting at yttrium (Z=39). This period ends at xenon with the filling up of the $5p$ orbitals. The sixth period (n=6) contains 32 elements and successive electrons enter $6s$, $4f$, $5d$ and $6p$ orbitals, in that order. Filling up of the $4f$ orbitals begins with cerium (Z=58) and ends at lutetium (Z =71) to give the $4f$-inner transition

series which is called the **Lanthanoid Series**. The seventh period (n=7) is similar to the sixth period with the successive filling up of the 7*s*, 5*f*, 6*d* and 7*p* orbitals and includes most of the man-made radioactive elements. This period will end at the element with atomic number 118 which would belong to the noble gas family. Filling up of the 5*f* orbitals after actinium (Z=89) gives the 5*f*-inner transition series known as the **Actinoid Series**. The 4*f*- and 5*f*- transition series of elements are placed separately in the periodic table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

(b) Groupwise/electronic configuration

Elements in the same vertical column or group have similar electronic configurations, have the same number of electrons in the outer orbitals, and similar properties. Group 1 (the alkali metals) is an example.

Thus it can be seen that the properties of an element have periodic dependence upon the atomic number and not on relative atomic mass.

Atomic number	Symbol	Electronic configuration
3	Li	$1s^2 2s^1$ or [He]$2s^1$
11	Na	$1s^2 2s^2 2p^6 3s^1$ or [Ne]$3s^1$
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or [Ar]$4s^1$
37	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$ or [Kr]$5s^1$
55	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$ or [Xe]$6s^1$

4.5 TYPES OF ELEMENTS : *s*-, *p*-, *d*-, *f*- BLOCKS

The *aufbau* principle (see Unit 3) and the electronic configuration of atoms provide a theoretical foundation for the periodic classification. The elements in a vertical column of the periodic table constitute a group or family and exhibit similar chemical behaviour. This similarity arises because these elements have the same number and same distribution of electrons in their outermost orbitals. We can classify the elements into four blocks *viz.* *s*-block, *p*-block, *d*-block and *f*-block depending on the type of atomic orbitals that are being filled with electrons. This is illustrated in Fig. 4.3. We notice two exceptions to this categorization. Strictly, helium belongs to the *s*-block but its positioning in the *p*-block along with other group 18 elements is justified because it has a completely filled valence shell ($1s^2$) and as a result, exhibits properties characteristic of other noble gases. The other exception is hydrogen. It has a lone *s*-electron and hence can be placed in group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. Because it is a special case, we shall place hydrogen separately at the top of the Periodic Table as shown in Fig. 4.2 and Fig. 4.3 (See Unit 11). We will briefly discuss the salient features of the four types of elements marked in the periodic table.

4.5.1 *s*-Block Elements

The elements of group 1 (alkali metals) and group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the **s-Block Elements**. They are all reactive metals with low ionization enthalpies (see Section 4.6.1). They lose the outermost electron(s) readily to form 1+ (in the case of alkali metals) or 2+ ions (in the case of alkaline earth metals). The metallic character and the reactivity increase as we go down the group. The compounds of the s-block elements, with the exception of those of beryllium are predominantly ionic.

4.5.2 The *p*-Block Elements

The ***p*-Block Elements** comprise those belonging to groups 13 to 18 and together with the *s*-block elements are called the **Representative Elements or Main Group Elements**. The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period. Each period ends in a noble gas with a closed shell ns^2np^6 configuration. All the orbitals in the valence shell of the **noble gases** are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Preceding the noble gas family are two chemically important groups of nonmetals. They are the **halogens** (group 17) and the **chalcogens** (group 16). These two groups of elements have high negative electron

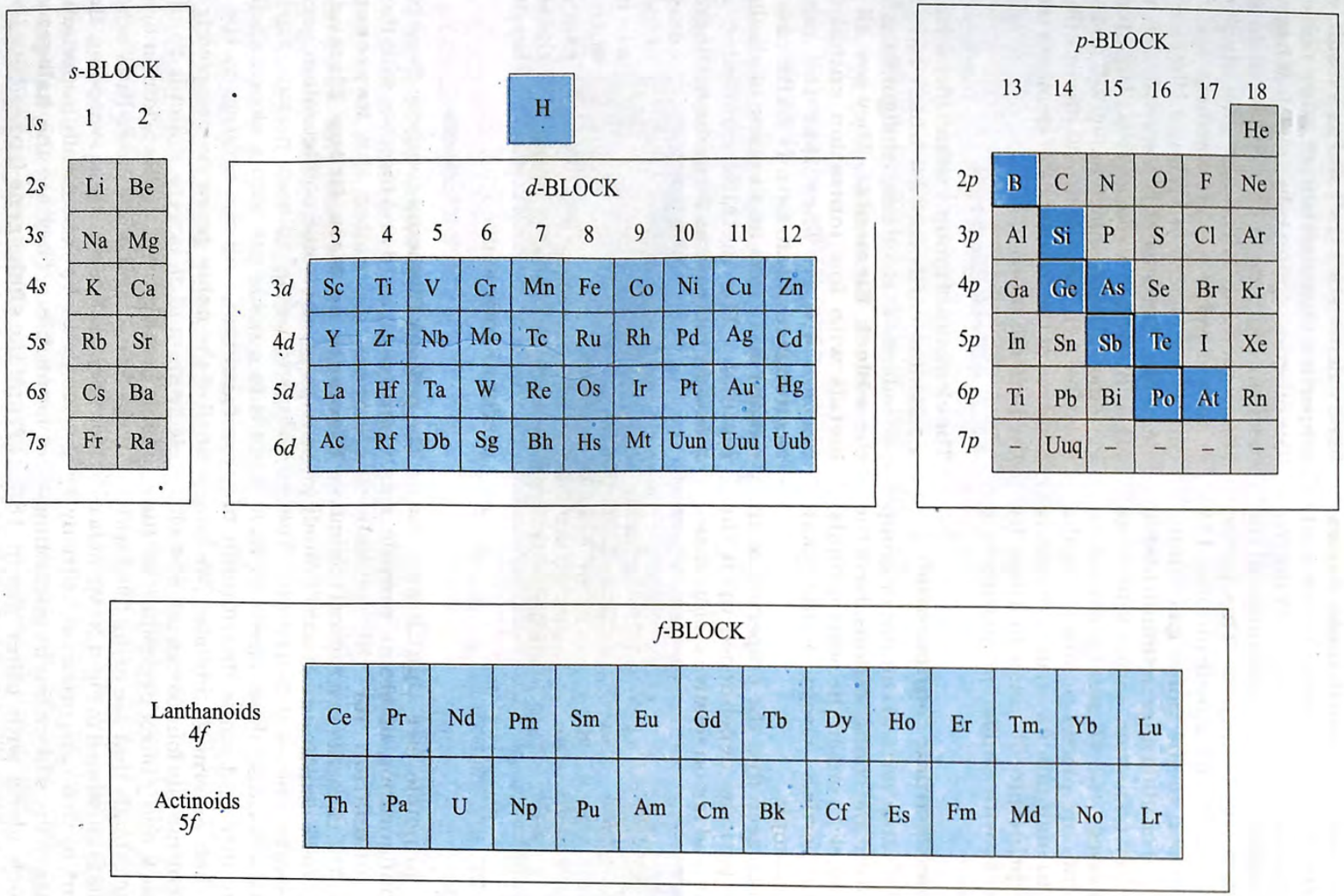
s-BLOCK
1s 1 2
2s Li Be
3s Na Mg
4s K Ca
5s Rb Sr
6s Cs Ba
7s Fr Ra
H
d-BLOCK
3 4 5 6 7 8 9 10 11 12
3d Sc Ti V Cr Mn Fe Co Ni Cu Zn
4d Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
5d La Hf Ta W Re Os Ir Pt Au Hg
6d Ac Rf Db Sg Bh Hs Mt Uun Uuu Uub
p-BLOCK
13 14 15 16 17 18
He
2p B C N O F Ne
3p Al Si P S Cl Ar
4p Ga Ge As Se Br Kr
5p In Sn Sb Te I Xe
6p Ti Pb Bi Po At Rn
7p – Uuq – – – –
f-BLOCK
Lanthanoids 4f Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinoids 5f Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

Fig. 4.3 *The types of elements in the Periodic Table based on the orbitals that are being filled. Also shown is the broad division of elements into METALS (on the left) and NON-METALS (on the right) marked by the thick zig-zag line. The elements on the border-line enclosed by the shaded squares are the METALLOIDS*

gain enthalpies (see Section 4.6.2) and readily add one or two electrons respectively to attain the stable noble gas configuration. The nonmetallic character increases as we move from left to right across a period and metallic character increases as we go down the group.

4.5.3 The d-block Elements (Transition Elements)

These are the elements of group 3 to 12 in the centre of the periodic table. These elements are characterized by the filling of inner *d* orbitals by electrons and are therefore referred to as ***d*-Block Elements**. These elements have the outer electronic configuration $(n-1)d^{1-10}ns^{1-2}$. They are all metals. They mostly form coloured ions and exhibit variable valency. However, Zn, Cd and Hg which have the $(n-1)d^{10}ns^2$ electronic configuration, do not show most of the properties of transition elements. In a way, transition metals form a bridge between the chemically active metals of *s*-block elements and the less active metals of groups 13 and 14 and thus take their familiar name "transition elements".

4.5.4 The f-Block Elements (Inner – Transition elements)

The two rows of elements at the bottom of the periodic table, called the **Lanthanoids** $_{58}Ce—_{71}Lu$ and **Actinoids**, $_{90}Th—_{103}Lr$ are characterized by the outer electronic configuration $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. The last electron added to each element is an *f*-electron. These two series of elements are hence called the inner transition elements (***f*-Block Elements**). They are all metals. Within each series, the properties of the elements are quite similar. The chemistry of the early actinoids is more complicated than the corresponding lanthanoids, due to the large number of oxidation states possible for these actinoid elements. Actinoid elements are radioactive. Many of the actinoid elements have been made only in nanogram quantities or less by nuclear reactions and their chemistry is not fully studied. The elements coming after uranium are called **transuranium** elements.

Example 4.2

The elements Z = 117 and 120 have not yet been discovered. In which family/group would you place these elements and also give the electronic configuration in each case.

Solution

We see from Fig. 4.1, that element with Z = 117, would belong to the halogen family (group 17) and the electronic configuration would be .

$[Rn]\ 5f^{14}6d^{10}7s^27p^5$

The element with Z = 120, will be placed in group 2 (alkaline earth metals), and will have the electronic configuration $[Uuo]8s^2$.

In addition to displaying the classification of elements into *s*-, *p*-, *d*-, and *f*-blocks, Fig.4.3 shows another broad classification of elements based on their properties. The elements can be divided into **Metals** and **Non-metals**. Metals comprise more than 75% of all known elements and appear on the left side of the Periodic Table. Metals are usually solids at room temperature (Mercury is an exception); they have high melting and boiling points. They are good conductors of heat and electricity. They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires). In contrast non-metals are located at the top right hand side of the Periodic Table. Non-metals are usually solids or gases at room temperature with low melting and boiling points. They are poor conductors of heat and electricity. Most non-metallic solids are brittle and are neither malleable nor ductile. The elements become more metallic as we go down a group; the non-metallic character increases as one goes from left to right across the Periodic Table. The change from metallic to non-metallic character is not abrupt as shown by the thick zig-zag line in Fig.4.3; the elements (e.g. germanium, silicon, arsenic, antimony and tellurium) bordering this line and running diagonally across the Periodic Table show properties that are characteristic of both metals and non-metals. These elements are called **Semi Metals** or **Metalloids**.

Example 4.3

Arrange the following elements in the increasing order of metallic character : Si, Be, Mg, Na, P.

Solution

Metallic character increases down a group and decreases along a period as we move from left to right. Hence the order of increasing metallic character is, P < Si < Be < Mg < Na.

4.6 PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

The periodic Law states that the properties of the elements vary periodically with their atomic numbers. The basis for this *periodicity* lies in the periodic repetition of the electronic configuration of the elements as the atomic number increases. Regular variations in physical and chemical properties are observed as we descend a group and move across a period in the Periodic Table. In this section, we shall discuss the periodic trends in three physical properties of the elements (ionization enthalpy, electron gain enthalpy and atomic size) and in one important chemical property, *viz. valence.*

4.6.1 Ionization Enthalpy

A quantitative measure of the tendency of an element to lose electron is given by its **Ionization Enthalpy**. It represents the energy required to remove an electron from an isolated gaseous atom (X) in its ground state. In other words, the first ionization enthalpy for an element X is the enthalpy change (ΔH) for the reaction depicted in Equation 4.1.

$$X(g) \rightarrow X^{+}(g) + e^{-}(g) \qquad (4.1)$$

The ionization enthalpy is expressed in units of kJ mol^{-1}. We can define the second ionization enthalpy as the energy required to remove the second most loosely bound electron; it is the energy required to carry out the reaction shown in Equation 4.2.

$$X^{+}(g) \rightarrow X^{2+}(g) + e^{-}(g) \qquad (4.2)$$

Energy is always required to remove electrons from an atom and hence ionization enthalpies are always positive. The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom. In the same way the third ionization enthalpy will be higher than the second and so on. The term "ionization enthalpy", if not qualified, is taken as the first ionization enthalpy.

The first ionization enthalpies of elements having atomic numbers upto 60 are plotted in Fig.4.4. The periodicity of the graph is quite striking. You will find maxima at the noble gases which have closed electron shells and very stable electron configurations. On the other hand, minima occur at the alkali metals and their low ionization enthalpies can be correlated with their high reactivity. In addition, you will notice two trends. The first ionization enthalpy generally increases as we go across a period and decreases as we descend the column of a group. These trends are illustrated in Fig.4.5(a) and 4.5(b) respectively for the elements of the second period. To understand these trends, we have to consider two factors : (i) the attraction of electrons to the nucleus, and (ii) the repulsion of electrons from each other.

The effective nuclear charge experienced by a valence electron in an atom will be less than the actual charge on the nucleus because of "**shielding**" or "**screening**" of the valence electron from the nucleus by the intervening core electrons. For example, the 2*s* electron in lithium is shielded from the nucleus by the inner core of 1s electrons. As a result, the valence electron experiences a net positive charge less than +3. In general shielding is effective when the orbitals in the inner shells are completely filled. This situation occurs in the case of alkali metals which have a lone *ns*-outermost electron preceded by a noble gas electronic configuration.

When we move from lithium to neon across the second period, successive electrons are added to orbitals in the same principal quantum level and the shielding of the nuclear charge by the inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. Thus, across a period, increasing nuclear charge outweighs the shielding. Consequently, the outermost electrons are held more and more tightly and the ionization enthalpy increases as we go across a period [see Fig.4.5(a)]. As we go down a group, the outermost electron being removed is farther from the nucleus and there is an increased shielding of the nuclear charge by the electrons in the inner levels. In this case, increase in shielding outweighs the increasing nuclear charge and the removal of the outermost electron requires less energy down a group [see Fig.4.5(b)].

From Fig.4.5(a), you will also notice that the first ionization enthalpy of boron (Z = 5) is slightly less than that of beryllium (Z=4) even though,

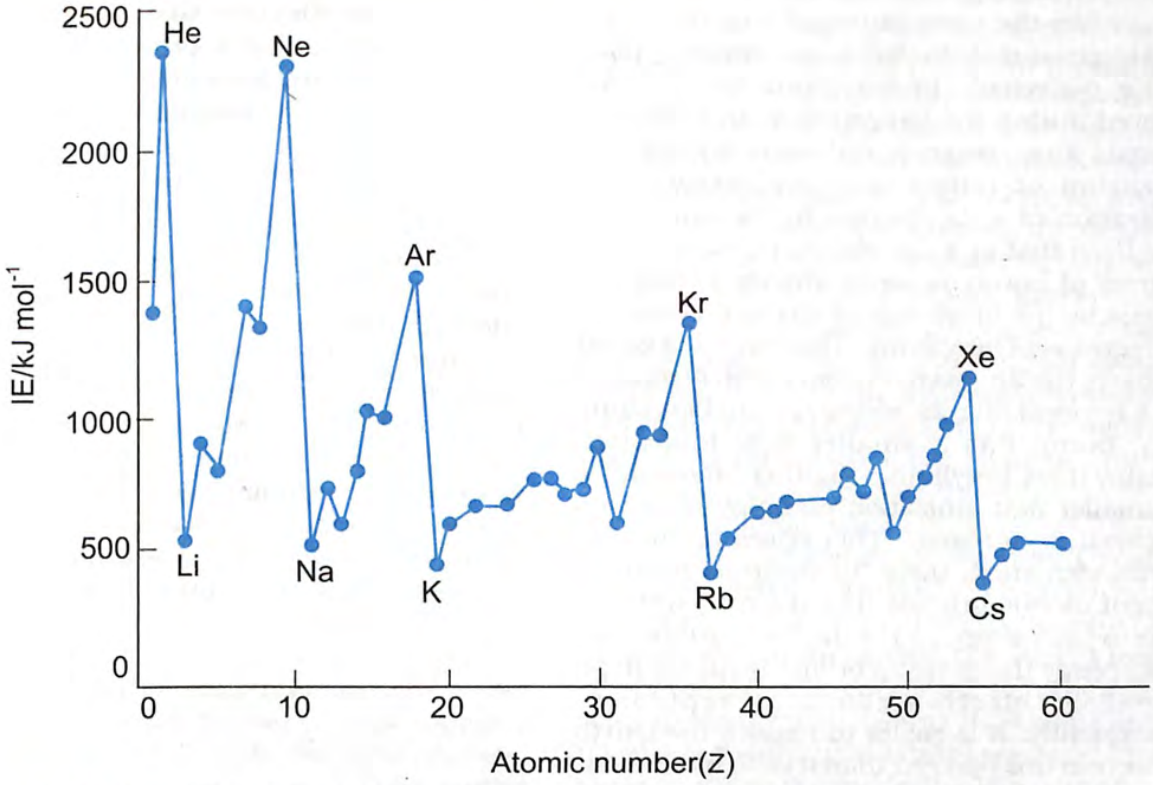

Fig.4.4 *Variation of first ionization enthalpies with atomic number for elements with Z = 1 to 60.*

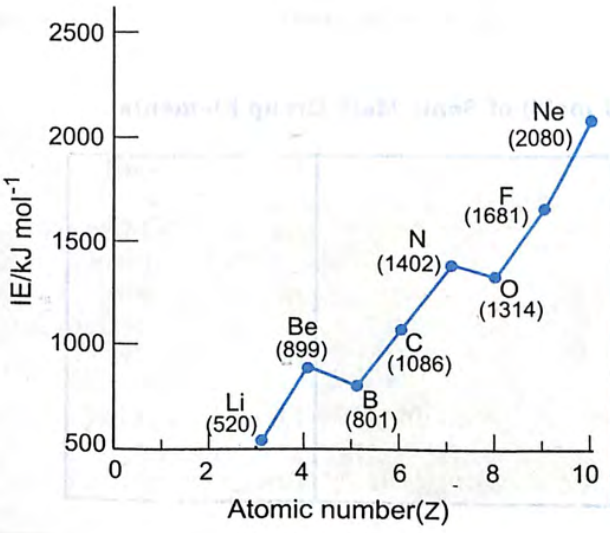

Fig.4.5 *(a)*

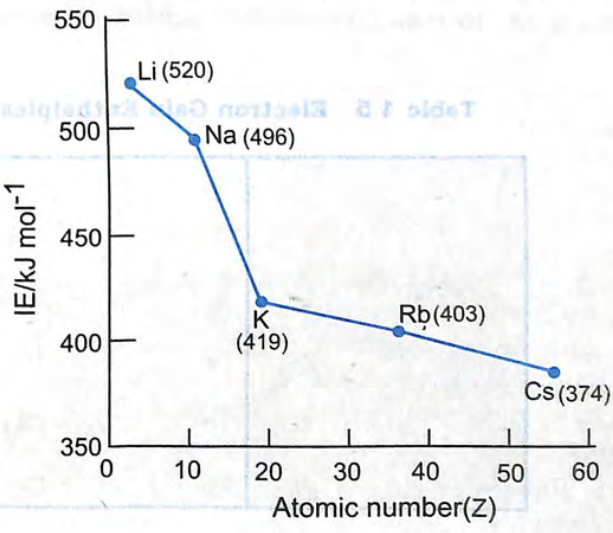

Fig.4.5 *(b)*

Fig.4.5 *(a) First ionization enthalpies of elements of the second period as a function of atomic number (b) First ionization enthalpies of alkali metals as a function of atomic number.*

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the former has a greater nuclear charge. When we consider the same principal quantum level, an *s*-electron is attracted to the nucleus more than a *p*-electron. In beryllium, the electron removed during the ionization is an *s*-electron whereas the electron removed during the ionization of boron is a *p*-electron. The penetration of a 2*s* electron to the nucleus is more than that of a 2*p* electron; hence the 2*p* electron of boron is more shielded from the nucleus by the inner core of electrons than the 2*s* electrons of beryllium. Therefore it is easier to remove the 2*p* electron from boron compared to the removal of a 2*s* electron from beryllium. Thus, boron has a smaller first ionization enthalpy than beryllium. Another "anomaly" is the smaller first ionization enthalpy of oxygen compared to nitrogen. This arises because in the nitrogen atom, three 2*p* electrons reside in different atomic orbitals (Hund's rule) whereas in the oxygen atom, two of the four 2*p* electrons must occupy the same 2*p* orbital resulting in an increased electron-electron repulsion. Consequently, it is easier to remove the fourth 2*p*-electron from oxygen than it is, to remove one of the three 2*p*-electrons from nitrogen.

4.6.2 Electron Gain Enthalpy ($\Delta_{eg}H$)[1]

When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the **Electron Gain Enthalpy** ($\Delta_{eg}H$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by equation 4.3.

$$X(g) + e^- \rightarrow X^-(g) ; \Delta H = \Delta_{eg}H. \qquad (4.3)$$

Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and the electron gain enthalpy is negative. For example, group 17 elements (the halogens) have very high negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron. On the other hand, noble gases have large positive electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration. It may be noted that electron gain enthalpies have large negative values toward the upper right of the periodic table preceding the noble gases. (see the values for O, F and Cl in Table 4.5).

The variation in electron gain enthalpies of elements is less systematic than for ionization enthalpies. As a general rule, electron gain enthalpy becomes more negative with increase

Table 4.5 Electron Gain Enthalpies /(kJ mol^{-1}) of Some Main Group Elements

H	- 73					He	+ 48
Li	- 60	O	- 141	F	- 328	Ne	+116
Na	- 53	S	- 200	Cl	- 349	Ar	+96
K	- 48	Se	- 195	Br	- 325	Kr	+ 96
Rb	- 47	Te	- 190	I	- 295	Xe	+77
Cs	- 46	Po	- 174	At	- 270	Rn	+68

[1] * In many books, the negative of the enthalpy change for the process depicted in equation 4.3 is defined as the ELECTRON AFFINITY (A_e) of the atom under consideration. If energy is released when an electron is added to an atom, the electron affinity is taken as positive, contrary to thermodynamic convention. If energy has to be supplied to add an electron to an atom, then the electron affinity of the atom is assigned a negative sign. However electron affinity is defined at absolute zero and therefore at any other temp^T.

heat capacities of the reactants and product have to be taken into account in $\Delta_{eg}H = -A_e - \frac{5}{2}RT$.

in the atomic number across a period. The effective nuclear charge increases as we go from left to right across a period and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. We should also expect electron gain enthalpy to become less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus. This is generally the case (Table 4.5). However, electron gain enthalpy of O or F is less than that of the succeeding element. This is because when an electron is added to O or F, the added electron goes to the smaller n = 2 quantum level and suffers significant repulsion from the other electrons present in this level. For the n=3 quantum level (S or Cl), the added electron occupies a larger region of space and the electron-electron repulsion is much less.

Example 4.4

Which of the following will have the most negative electron gain enthalpy and which the least negative ?
P, S, Cl, F.
Explain your answer.

Solution

Electron gain enthalpy generally becomes more negative across a period as we move from left to right. Within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the 2*p* orbital leads to greater repulsion than adding an electron to the larger 3*p* orbital. Hence the element with most negative electron gain enthalpy is chlorine; the one with the least negative electron gain enthalpy is phosphorus.

4.6.3 Atomic and Ionic Radii

The size of an atom cannot be determined precisely as the electron cloud surrounding the atom does not have a sharp boundary. In other words, there is no practical way by which the size of an individual atom can be measured. However, an estimate of the atomic size can be made by knowing the distance between the atoms in the combined state. One practical approach to estimating the size of an atom of a non-metallic element is to measure the distance between two atoms when they are joined together by a single bond in a covalent molecule and from this value, the "**Covalent Radius**" of the element can be calculated. For example, the bond distance in the chlorine molecule (Cl_2), is 198 pm and half this distance (99 pm), is taken as the atomic radius of chlorine. For metals, we define the term "**Metallic Radius**" which is taken as half the internuclear distance separating the metal ions in the metallic crystal. For example, the distance between two adjacent copper atoms in solid copper is 256 pm; hence the metallic radius of copper is assigned a value of 128 pm. For simplicity, in this book, we use the term **Atomic Radius** to refer to both covalent or metallic radius depending on whether the element is a non-metal or a metal (See also Unit 6).

The atomic radii of a few elements are listed in Table 4.6. Two trends are obvious. The atomic size decreases across a period as illustrated in Fig. 4.6(a) for the elements of the second period because within the period the outer electrons are in the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus. The same feature causes the ionization enthalpies to increase from left to right across a period (Section 4.6.1). Within a family or vertical column of the **periodic table**, the atomic radius increases regularly with atomic number as illustrated in Fig.4.6(b) for alkali metals and halogens. As we descend a group, the principal quantum number (*n*) increases and the valence electrons are farther from the nucleus. Consequently the size of the atom increases as reflected in the atomic radii.

We can also define another set of radii called the "**Ionic Radii**" which can be estimated by measuring the distances between cations and anions in ionic crystals. In general, the ionic radii of elements exhibit the same trend as the atomic radii. A cation is smaller than its parent atom because it has fewer electrons while its nuclear change remains the same. The size of an anion (negative ion) will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. For example, the ionic radius of fluoride ion (F^-) is 136 pm where as the atomic radius of fluorine is only 72 pm.

Table 4.6(a) Atomic Radii/pm Across the Periods

Atom	Atomic radius	Atom	Atomic radius
Li	152	Na	186
Be	111	Mg	160
B	88	Al	143
C	77	Si	117
N	70	P	110
O	74	S	104
F	72	Cl	99

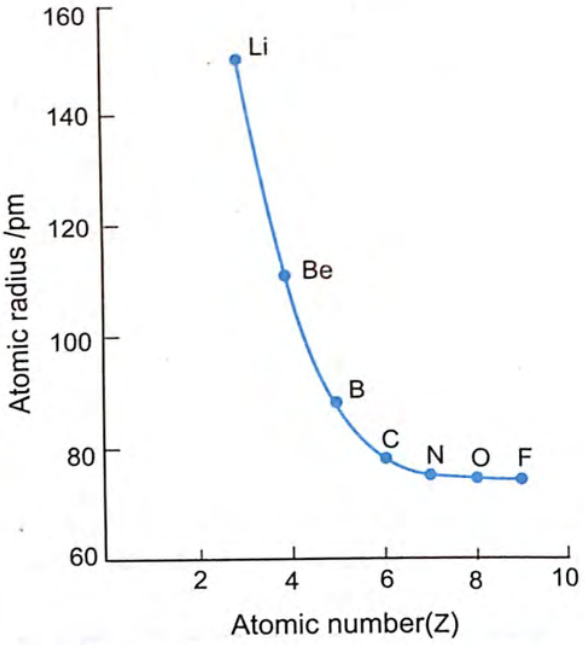


Fig.4.6 (a) *Variation of atomic radius with atomic number across the second period*

Table 4.6(b) Atomic Radii/pm Down the Group Across a Family

Atom	Atomic radius	Atom	Atomic radius
Li	152	F	72
Na	186	Cl	99
K	231	Br	114
Rb	244	I	133
Cs	262	At	140

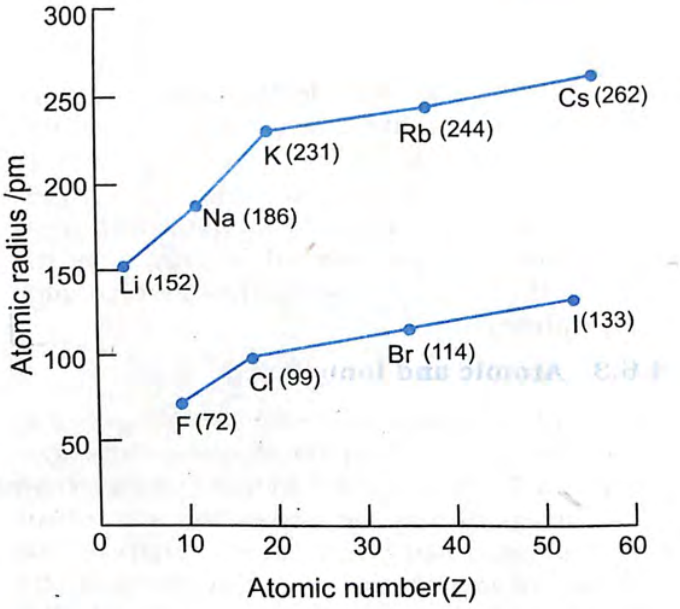


Fig.4.6 (b) *Variation of atomic radius with atomic number for alkali metals and halogens*

On the other hand, the atomic radius of sodium is 186 pm compared to the ionic radius of 95 pm for Na^+.

When we find some atoms and ions which contain the same number of electrons, we call them **isoelectronic**. For example, O^{2-} F^-, Na^+ and Mg^{2+} have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anions with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size.

Example 4.5

Which of the following species will have the largest and the smallest size?
Mg, Mg^{2+}, Al, Al^{3+}.

Solution

Atomic radii decrease across a period. Cations are smaller than their parent atoms. Among isoelectronic ions, the one with the larger positive nuclear charge will have a smaller radius.

Hence the largest species is Mg; the smallest one is Al^{3+}.

Periodicity of Valence

We can understand the valence of the elements in terms of their electron configurations. The valence of representative elements is usually equal to the number of electrons in the outermost orbitals and/or equal to eight minus the number of outermost electrons. Some periodic trends observed in the valence of elements (hydrides and oxides) are shown in Table 4.7. Other such periodic trends which occur in the chemical behaviour of the elements are discussed elsewhere in this book. There are many elements which exhibit variable valence. This is particularly characteristic of transition elements.

Example 4.6

Using the Periodic Table, predict the formulae of compounds which might be formed by the following pairs of elements; (a) silicon and bromine (b) aluminium and sulphur.

Solution

(a) Silicon, is group 14 element with a valence of 4; bromine belongs to the halogen family with a valence of 1. Hence the formula of the compound formed would be $SiBr_4$.

(b) Aluminium belongs to group 13 with a valence of 3; sulphur belongs to group 16 elements with a valence of 2. Hence the formula of the compound formed would be Al_2S_3.

Table 4.7 Periodic Trends in Valence of Elements as Shown by the Formulae of their Compounds

Group	1	2	13	14	15	16	17
Formulae of hydrides	LiH NaH KH			CH_4 SiH_4 GeH_4 SnH_4	NH_3 PH_3 AsH_3 SbH_3	H_2O H_2S H_2Se H_2Te	HF HCl HBr HI
Formulae of oxides	Li_2O Na_2O K_2O	MgO CaO SrO BaO	B_2O_3 Al_2O_3 Ga_2O_3 In_2O_3	CO_2 SiO_2 GeO_2 SnO_2 PbO_2			

SUMMARY

Mendeleev's **Periodic Table** was based on atomic masses. Modern Periodic Table arranges the elements in the order of their atomic numbers and better still according to their electron configuration. The elements in the same column exhibit similar chemical properties and constitute a **family** or **group**; the horizontal rows are called **periods**. The electron configuration of elements and the **aufbau** principle provide a basis for periodic classification. Four types of elements can be recognized in the Periodic Table depending on the types of orbitals that are being filled. These are ***s*-block, *p*-block, *d*-block** and ***f*-block** elements. **Hydrogen** with one electron in the 1*s* orbital occupies a unique position in the Periodic Table. **Metals** comprise more than seventy five per cent of the known elements. There are about twenty **non-metals** which are located at the top right of the Periodic Table. Elements which lie at the borderline between metals and non-metals (e.g., Si, Ge, As) are called **semimetals** or **metalloids**. Metallic character increases as we go down a group. Non-metallic character increases across a period. The chemical and physical properties of elements vary periodically with their atomic numbers. **Periodic trends** are observed in **ionization enthalpies, electron gain enthalpies, atomic sizes** and **valence** of elements. The **first ionization enthalpy** is the enthalpy change for the reaction : $X(g) \rightarrow X^{+}(g) + e^{-}(g)$. Ionization enthalpies generally increase across a period and decrease down a group. **Electron gain enthalpy** is the enthalpy change accompanying the addition of an electron to a gaseous atom of the element represented by the reaction : $X(g) + e^{-}(g) \rightarrow X^{-}(g)$. In general, electron gain enthalpies become more negative across a period and less negative down a group. **The atomic or covalent radius** is defined as one-half the distance between the nuclei of two atoms in a diatomic or polyatomic molecule of an element or between two metal atoms in a metallic solid. The atomic radius decreases from left to right across a period and within a group increases with increase in atomic number. **Valence** can be defined as the number of atoms of hydrogen (or twice the number of oxygen) required by one atom of the element to form a stable compound. There is some periodicity in **valence**; for example, among representative elements, the valence is either equal to the number of electrons in the outermost orbitals or eight minus this number.

EXERCISES

4.1 Which important property did Mendeleev use to classify the elements in his Periodic Table ?

4.2 State the modern "Periodic Law'.

4.3 Explain the terms 'ionization enthalpy' and 'electron gain enthalpy'.

4.4 Predict which atom in each of the following pairs has the greater first ionization enthalpy and explain your answer :
(a) B and C (b) N and O (c) F and Ne

4.5 Among the elements Li, K, Ca, S and Kr, which one is expected to have the lowest first ionization enthalpy and which the highest first ionization enthalpy ?

4.6 Among the elements of the third period Na to Ar pick out the element
(i) with the highest first ionization enthalpy (ii) with the largest atomic radius
(iii) that is the most reactive non-metal (iv) that is the most reactive metal.

4.7 Which of the following pairs of elements would you expect to have lower first ionization enthalpy ? Explain.
(i) Cl or F (ii) Cl or S (iii) K or Ar (iv) Kr or Xe

4.8 Why does the first ionization enthalpy increase as we go from left to right across a given period of the Periodic Table ?

4.9 Explain why ionization enthalpies decrease down a group of the Periodic Table.

4.10 Which of the following pairs of elements would have a more negative electron gain enthalpy? Explain.
(i) N or O , (ii) F or Cl.

4.11 Name a species that will be isoelectronic with each of the following atoms or ions:
(i) Ne (ii) Cl^- (iii) Ca^{2+} (iv) Rb

4.12 How do atomic sizes vary in a group and in a period ? Give reasons for the variations.

4.13 In each of the following pairs, which species has a larger size ? Explain.
(i) K or K^+ (ii) Br or Br^- (iii) O^{2-} or F^- (iv) Li^+ or Na^+ (v) P or As (vi) Na^+ or Mg^{2+}

4.14 Arrange the following ions in the order of increasing size :
Be^{2+}, Cl^-, S^{2-}, Na^+, Mg^{2+}, Br^-

4.15 The first ionization enthalpy of magnesium is higher than that of sodium. On the other hand, the second ionization enthalpy of sodium is very much higher than that of magnesium. Explain.

4.16 From each set, choose the atom which has the largest ionization enthalpy and explain your answer
(a) F, O, N, (b) Mg, P, Ar, (c) B, Al, Ga

4.17 Select from each group the species which has the smallest radius stating appropriate reason.
(a) O, O^-, O^{2-}, (b) K^+, Sr^{2+}, Ar (c) Si, P, Cl

4.18 Lanthanoids and actinoids are placed in separate rows at the bottom of the Periodic Table. Explain the reason for this arrangement.

4.19 Describe the main characteristic properties of *s*, *p*, *d* and *f*-block elements.

4.20 Arrange the following elements in the increasing order of metallic character.
B, Al, Mg, K.

4.21 Arrange the following elements in the increasing order of non-metallic character.
B, C, Si, N, F

4.22 Predict the position of the element in the Periodic Table satisfying the electron configuration $(n-1)d^1ns^2$ for n=4.

4.23 Elements A,B,C,D and E have the following electronic configurations :
A : $1s^2 2s^2 2p^1$ B : $1s^2 2s^2 2p^6 3s^2 3p^1$
C : $1s^2 2s^2 2p^6 3s^2 3p^3$ D : $1s^2 2s^2 2p^6 3s^2 3p^5$
E : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Which among these will belong to the same group in the periodic table?

4.24 The first (IE_1) and the second (IE_2) ionization enthalpies (kJ mol^{-1}) of a few elements designated by Roman numerals are shown below :

Element	IE_1	IE_2
I	2372	5251
II	520	7300
III	900	1760
IV	1680	3380

Which of the above elements is likely to be
(a) a reactive metal
(b) a reactive non-metal
(c) a noble gas
(d) a metal that forms a stable binary halide of the formulae AX_2 (X = halogen)

4.25 The first (IE_1) and the second (IE_2) ionization enthalpies (kJ mol^{-1}) of three elements I, II and III are given below:

	I	II	III
IE_1	403	549	1142
IE_2	2640	1060	2080

Identify the element which is likely to be
(a) a non-metal (b) an alkali metal (c) an alkaline earth metal

4.26 The element 119 has not been discovered. What would be the IUPAC name and symbol for this element? On the basis of the Periodic Table, predict the electronic configuration of this element and also the formula of its most stable chloride and oxide.

4.27 Predict the formulae of the stable binary compounds that would be formed by the following pairs of elements.
(a) silicon and oxygen (b) aluminium and bromine
(c) calcium and iodine (d) element 114 and fluorine
(e) element 120 and oxygen

4.28 Among the elements B, Al, C and Si,
(a) which has the highest first ionization enthalpy ?
(b) which has the most negative electron gain enthalpy ?
(c) which has the largest atomic radius ?
(d) which has the most metallic character ?

4.29 Consider the elements N, P, O and S and arrange them in order of
(a) increasing first ionization enthalpy ?
(b) increasing negative electron gain enthalpy ?
(c) increasing non-metallic character

4.30 Which of the elements Na, Mg, Si and P would have the greatest difference between the first and second ionization enthalpies. Briefly explain your answer.

UNIT 5

First Law of Thermodynamics and Chemical Energetics

Objectives

After studying this Unit, you will be able to

- explain the terms: system, surroundings, work and energy.
- distinguish among close, isolated and open systems.
- state first law of thermodynamics and express it mathematically.
- identify the nature of energy changes in chemical reactions.
- correlate heat absorbed at constant volume with change in internal energy(ΔU), and heat absorbed at constant pressure with change in enthalpy(ΔH).
- learn how to measure changes in internal energy (ΔU) and enthalpy (ΔH).
- define standard state for enthalpy change.
- determine enthalpy change for phase transformations.
- state and apply Hess's law of constant heat summation.
- calculate *bond enthalpy* with the help of enthalpy changes and vice versa.
- name different sources of energy and state their importance in daily life.

"Hot and cold are Nature's two hands with which she cheerfully works"

Our energy needs are met by burning fossil fuels and more recently from nuclear reactions. These processes produce heat which can be converted into mechanical energy to operate a machine or propel a vehicle. Transformation of heat into work is achieved by the use of devices called engines. The engines use the energy stored in a fuel to perform mechanical work, to drive, for example, an electric generator, an automobile or a ship.

Thermodynamics deals with energy in its various forms and their interconversion. The scope of thermodynamics is very large. Chemical processes release stored energy as heat, work, or both. These quantities (heat and work) are linked through the **first law of thermodynamics**. How much heat can be converted into useful work is governed by the **second law of thermodynamics**. There are two other laws of thermodynamics – Third law and Zeroth law. We will discuss zeroth law and first law in this Unit. The second and third laws will be covered in Class XII. The importance of thermodynamics lies in the fact that it provides explanation of macroscopic (bulk) properties of matter especially the thermal properties consistent with our *microscopic* views of a material world made up of atoms and molecules. Almost all chemical reactions occur with either absorption or release of energy. It is important to have *quantitative* information about the energy changes associated with chemical reactions. This aspect is dealt under **Chemical Energetics**. Before undertaking the study of the first law of thermodynamics including chemical energetics, we will try to understand concept of temperature and discuss the statement of zeroth law and its implications and then define some of the terms required in the study of thermodynamics.

5.1 SOME BASIC CONCEPTS IN THERMODYNAMICS

5.1.1 Thermodynamic Scale of Temperature

In our daily life, we come across various objects having different degree of hotness according to our physical senses. In order to understand this vague idea of hotness or coldness, we need to define a recognisable temperature scale and make all measurements of hotness with reference to it. In celsius scale, for example, we have the familiar reference points, the ice point (0°C) and the steam point (100°C) for water, with the interval between them divided into 100 parts called degrees. The kelvin scale has been universally adopted since 1954 by the **international committee on weights and measures**. It is based on the absolute zero of temperature and the **triple point**[1] **of water**, which corresponds to a fixed temperature and pressure (namely 4.58 torr and 0.01°C) at which ice, water, and water vapour all exist in equilibrium. The basic SI unit of temperature is Kelvin (K). One kelvin is $\frac{1}{273.16}$ of the triple point temperature of water (273.16 K). This scale is called *thermodynamic temperature scale*. It is an absolute scale (having as its zero point the lowest possible temperature), whereas the celsius scale is a relative scale whose zero point is the arbitrary creation of its inventor. In all thermodynamic calculations and in most of the calculations involved in other Units of this book, we will use kelvin scale of temperature.

5.1.2 Zeroth Law of Thermodynamics

When two objects maintained at different temperatures are brought in thermal contact, they exchange heat with each other until they reach a state of thermal equilibrium and after that no further exchange of energy takes place between them. At this point, temperature of the two objects is the same. If one of these objects happens to be a thermometer, the reading on the thermometer should become constant and calibration mark should give the temperature of the object. These ideas are expressed in the form of **law of temperature or thermal equilibrium**, which is also known as the **zeroth law of thermodynamics.**

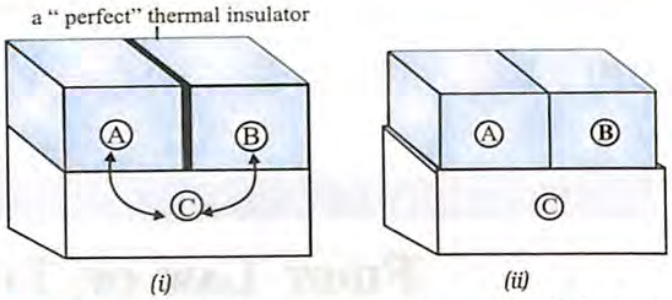


Fig 5.1 *Zeroth law of thermodynamics. (i) If A and B are in thermal equilibrium with (C) they are (ii) in thermal equilibrium with each other.*

The zeroth law can be summarized in following ways:

- Two objects at different temperatures in thermal contact with each other tend to move towards the same temperature.
- Two objects in thermal equilibrium with the third one, are in thermal equilibrium with each other (Fig.5.1).

5.1.3 System

The word *system* is very commonly used in thermodynamics. The **thermodynamic system** refers to any part of the real world under study. Everything that is not part of the system and can interact with it is called **surroundings**. For example, if we study the reaction between two substances A and B, the reaction mixture of A and B constitutes this system. All the rest (i.e. beaker in which the mixture is kept, the room where the beaker is kept) are parts of the surroundings. A system and its surroundings are always separated by boundaries (real or imaginary) across which matter and energy may be exchanged. The surroundings can affect the system by the transfer of matter or energy.

*A system is said to be **isolated** if it cannot exchange matter and energy with surroundings.* There is no perfectly isolated system; but a system which is thermally well insulated (i.e. does not allow heat flow) and is sealed to inflow or outflow of matter can be considered as an **isolated system**. Coffee in a stoppered thermos flask can be considered as an example of an isolated system ('a' in Fig.5.2A). The stopper prevents water vapour from escaping while the vacuum construction prevents heat from being lost to the surroundings. *A system is said to be **closed**, if it can exchange energy* (heat or work)

1 *A temperature at which all the phases: ice, liquid water and vapour coexit and are in equilibrium.*

but not matter. Coffee in a closed steel flask ('b' in Fig.5.2A) is an example of a closed system because energy can be gained or lost through the steel walls but not the matter. *An* ***open system*** *can exchange or transfer matter and/or energy between system and surroundings.* A tumbler of coffee ('c' in Fig.5.2A) is an open system. There can be, transfer of heat and water vapour (matter) with the surroundings. All living systems are open systems because they are continuously exchanging matter and energy with the surroundings. Fig.5.2B illustrates the characteristics of different types of systems.

Fig 5.2A *Examples of (a) isolated, (b) closed and (c) open systems*

5.1.4 State of a Macroscopic System

The ***state***[2] *of a thermodynamic system is described by its measurable or macroscopic properties.* We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T are called **state variables** or **state functions** because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the properties of the system as only a certain number of properties can be varied independently. The number depends on the nature of the system. Once these minimum number of macroscopic properties are fixed, others automatically have definite values. State functions are very useful because change in their values depends only on the **initial and final states** of the system and not on how change is carried out. *A system in a state of thermodynamic equilibrium*[3] *is one in which the macroscopic properties do not change with time.* The **initial state** of the system refers to the starting state of a system in equilibrium, prior to the onset of some kind of interaction with the surroundings. In **final state** the system attains equilibrium after interaction with the surroundings. The interaction with the surroundings means transfer of matter or energy or both.

5.1.5 Thermodynamic Processes

When a thermodynamic system undergoes a change of state, we say it has undergone a **process**. The process may be accompanied by an exchange of matter and energy between the system and surroundings. Thus, a process means change in at least one of the state variables of the system. The path of a process consists of the series of thermodynamic states

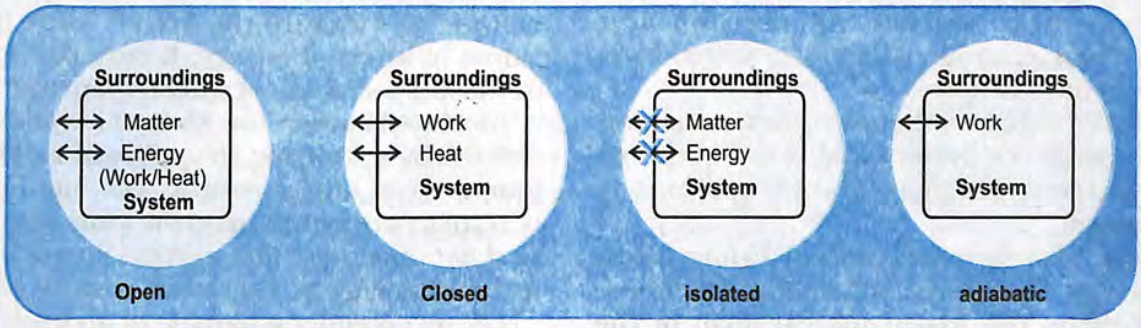


Fig.5.2B *Illustration of the characteristics of different types of systems*

2 *Here 'state' should not be confused with 'phase'.*

3 *We shall study here only 'equilibrium thermodynamics'. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure, temperature and concentration do not change with time for a system in equilibrium state. In* ***'chemical equilibrium'*** *which you will study in Unit 7, concentration of the reactants and products also do not change with time.*

through which the system passes on its way from the *initial state* to *final state*. Processes starting with the same initial state and ending at a particular final state going through different paths correspond to different processes. There are certain processes in which a particular state variable (thermodynamic property of the system) remains unchanged. Such processes are identified with special nomenclature.

A process is called **isothermal**, if the temperature of the system remains constant during the change. A process is called **adiabatic**, (Fig.5.2B) if the system does not exchange heat with the surroundings. An adiabatic process may involve increase or decrease in temperature of the system. Systems in which such processes occur, are thermally insulated from the surroundings. A very important type of process is called **reversible process** wherein the change is carried out so slowly that system and surroundings are always in near equilibrium[4]. Such states are called quasi-equilibrium state. Processes other than reversible processes are **irreversible processes**. There are processes in which p or V are kept constant and these are called **isobaric** and **isochoric** processes respectively.

5.2 FIRST LAW OF THERMODYNAMICS

The *first law of thermodynamics* is identical to the *law of conservation of energy*. It can be stated in many ways but the following statements are useful to us :

(i) Energy can neither be created nor destroyed although it can be changed from one form to another.
(ii) The total energy of the universe is constant.
(iii) The energy of a system that is isolated from its surroundings (isolated system) is constant.

The first law provides useful information about energy changes in chemical reactions. Before deriving the mathematical form of the first law of thermodynamics, it would be relevant to know about *internal energy* and how internal energy is affected by *work* and *heat* changes.

5.2.1 Heat, Work and Internal Energy

Heat is a form of energy. Although the two have the same units (joule), but these are not synonymous. Heat flows from one system to another as a result of a difference in temperature, and it is basically *energy on the move*. Energy is exchanged between a system and its surroundings by heat transfer. For example, if we keep a beaker filled with hot water (at 65°C) in open, within a few minutes it will cool down and will attain a thermal equilibrium with the surroundings. In other words, finally the temperature of the system (i.e. water in beaker) and the surroundings will be the same. The energy of a thermodynamic system under given condition is called **internal energy**. Internal energy is made up of kinetic and potential energies of the constituent particles. The kinetic energy arises due to the motions of all the particles. (This includes their translation, rotation and vibration etc).The potential energy arises from different type of interactions between the particles. This includes interaction between the electrons and the nuclei in atoms and molecules and the interaction energy of the constituent molecules in the system.

The kinetic energy is a function of temperature i.e., higher the temperature, greater is the kinetic energy. Internal energy changes when heat is transferred from system to surroundings or from surroundings to system. According to the first law of thermodynamics, the internal energy (denoted by U) of an isolated system is constant. The first law, however, does not provide any method to measure the actual value (absolute value) of internal energy; it only provides ways to measure *change* of internal energy, ΔU.

As stated earlier, the state of a system can be defined by specifying the value of variables like temperature and pressure. *The internal energy of a system depends upon the state of the system and not upon how the system attains that state.* Internal energy is, therefore, a *state function*.

Let us consider a sample of an ideal gas that occupies a volume of 1 litre at 100K and 1 atm pressure (state A). At 200K and 0.5 atm (state B), the gas occupies a volume of 4 litres. Let us denote internal energies in state A and B by U_A

4 *For bringing any change in the system in equilibrium, the system has to be disturbed. However, this disturbance may be so small that the system is nearly in equilibrium. Such states are called quasi equilibrium states.*

and U_B, respectively. According to the first law of thermodynamics, the internal energy, U_A in state A and the internal energy, U_B in state B have definite values and, therefore, their difference, ΔU, will be independent of the path taken between state A and state B. It makes no difference whether the gas is heated before the pressure change or whether the heating is done after the pressure change, or, whether the total change is brought about in several steps; the change in internal energy, ΔU, in every case is the same because the initial and final states are characterized by U_A and U_B.

The internal energy of a system can be changed in two ways, (i) either by allowing *heat* to flow into the system or out of the system and (ii) by *work* done on the system or by the system. Let us consider a system whose internal energy is U_1. If the system is supplied q amount of heat, the internal energy of the system increases to U_1+ q. If work (w) is now done on the system, the internal energy in the final state of the system, U_2, is given by

$$U_2 = U_1 + q + w \qquad (5.1)$$

or $U_2 - U_1 = q + w$

or $\Delta U = q + w \qquad (5.2)$

This relationship between internal energy, work and heat is a *mathematical statement of the first law of thermodynamics.*

It should be noted that q and w are not state functions. Work and heat are called as energy in transition and have their role only during the process. This is why values of q and w depend upon the way the processes are carried out. The essence of Eq. 5.2 is that though individually q and w are not state functions but q + w (= ΔU) does not depend upon how the change is brought about and hence independent of the path. The net change in internal energy, that is (q + w) depends only on the initial and final states.

If a system undergoes a change in which internal energy of the system remains constant (i.e, $\Delta U = 0$), then – w = q. This means that work done *by* the system equals the heat absorbed by the system. In other words whatever heat was absorbed by system was used in doing work.

Work can be performed in a number of ways but we shall normally come across chemical systems involving *electrical work* and/or *mechanical work*. Electrical work is important in systems where there is transport of ions under electrical potential while mechanical work

Sign Convention for q and w

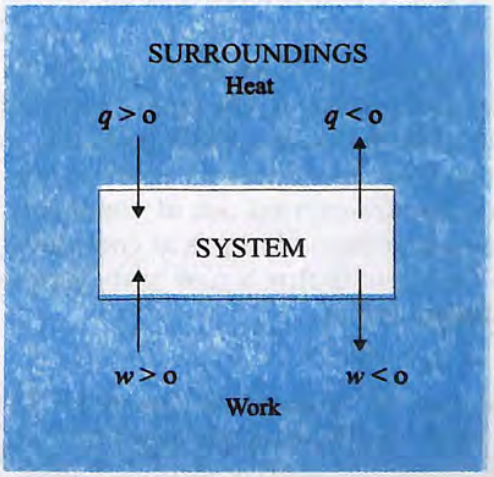
Let us illustrate the sign convention of q and w. If we supply 20 kJ of heat to the system, we write q = 20 kJ, but if the same quantity of heat is transferred to the surroundings from the system, we would write q = - 20 kJ (since there is loss of energy of the system).

When work is done on the system, the energy of the system increases. Suppose we transfer 10 kJ of energy to the system by doing work on it, we would write, w = 10 kJ. But if system does work (on the surroundings) it will do so at the cost of its internal energy and it will lose 10 kJ of energy. Here we would write w = -10 kJ.

When w or q is positive, it means that energy has been supplied to the system as work or as heat. The internal energy of the system in such a case increases. When w or q is negative, it means that energy has been lost by the system as work or as heat. The internal energy of the system in such a case decreases.

To summarise, when

heat is absorbed by the system, q is positive;
heat is evolved by the system, q is negative;
work is done on the system, w is positive;
work is done by the system, w is negative.



is performed when a system changes its volume against external pressure.

Mechanical work is specially important in systems that contain *gases*. In certain reactions involving gases, volume changes occur at constant atmospheric pressure. If the system expands during the reaction, there will be pressure-volume work. If pressure p is constant and the volume changes from V_i to V_f, the work done by the system is given by

$$w = -p\,(V_f - V_i) = -p\Delta V$$

In fact, this equation is applicable for expansion as well as compression, of a gas. When a gas expands $(V_f - V_i) > 0$ and $-p\Delta V$ is a negative quantity; the system does work on its surroundings, so w is negative. When gas is compressed, $(V_f - V_i) < 0$ and $-p\Delta V$ is a positive quantity; surroundings do work on the system, so w is positive. Now if we substitute $p\Delta V$ for w in equation (5.2), we get

$$\Delta U = q - p\Delta V \qquad (5.3)$$

If a process is carried out at constant volume (i.e. $\Delta V = 0$) then

$$\Delta U = q_V \qquad (5.4)$$

(The subscript v in q_V denotes that volume is held constant).

Equation 5.4 shows that one can determine ΔU by measuring the heat absorbed at *constant volume*. For measuring the amount of heat transferred at constant volume, reaction must be carried out in a closed, rigid container with constant volume. For this reason, measurement of heat at constant volume is done in **Bomb calorimeter** (Sec. 5.4).

5.2.2 Enthalpy

For a process or a chemical reaction carried out at constant volume, the heat absorbed/evolved is equal to the corresponding change in internal energy (ΔU). In chemistry most of the chemical reactions are carried out at constant pressure. To measure heat changes at constant pressure, it is useful to define a new state function called **enthalpy** (H) as

$$H = U + pV \qquad (5.5)$$

It can be seen from equation 5.5 that H depends on three state functions U, p and V and hence it is also a state function.

From the definition of H, it follows that change in enthalpy (ΔH) is given by

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + p\Delta V + V\Delta p \qquad (5.6)$$

If the change takes place at constant pressure, (i.e. $\Delta p = 0$) then

$$\Delta H = \Delta U + p\Delta V \text{ (at constant pressure)} \qquad (5.7)$$

Substituting, Equation 5.3 in 5.7, we get

$$\Delta H = q \quad \text{(at constant pressure)}$$

$$\text{or } \Delta H = q_p \qquad (5.8)$$

where the symbol q_p has been introduced to indicate heat absorbed at constant pressure. Enthalpy changes for some reactions can be measured very conveniently using coffee-cup calorimeter (Fig 5.5). Equation (5.8) is important because it shows that *when we measure heat change at constant pressure, we are actually measuring change in the enthalpy*. In calorimeters operating at constant pressure, the enthalpy change of a process can be determined directly.

The difference between ΔH and ΔU is not usually significant for systems consisting of only solids and/or liquids. The difference, however, becomes significant when gases are involved. Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law we write,

$$pV_A = n_A RT$$

and $$pV_B = n_B RT$$

Thus, $$pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A)\,RT$$

or $$p\,(V_B - V_A) = (n_B - n_A)\,RT$$

or $$p\Delta V = \Delta n_g RT \qquad (5.9)$$

Here, Δn_g refers to the number of moles of **gaseous products** minus the number of moles of **gaseous reactants**.

We know that at constant pressure

$$\Delta H = \Delta U + p\Delta V$$

Therefore,

$$\Delta H = \Delta U + \Delta n\,RT \qquad (5.10)$$

The above equation is useful for calculating ΔH from ΔU and vice versa.

Pressure -Volume work

For understanding pressure-volume work let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p (Fig.5.3a). If external pressure is p_{ex} which is slightly greater than p (i.e $p_{ex} > p$), piston is moved downwords till the pressure inside becomes equal to p_{ex} (Fig. 5.5b). During this compression, suppose piston moves a distance, d and if cross-sectional area of the piston is A.

Volume change = d × A = $\Delta V = (V_f - V_i)$

We also know, pressure = $\frac{\text{force}}{\text{area}}$

Therefore, force on the piston = p_{ex} . A

If w is the work done on the system by movement of the piston then

w = force × distance = p_{ex} . A .d

= p_{ex} . $(-\Delta V) = - p_{ex} \Delta V = - p_{ex} (V_f - V_i)$

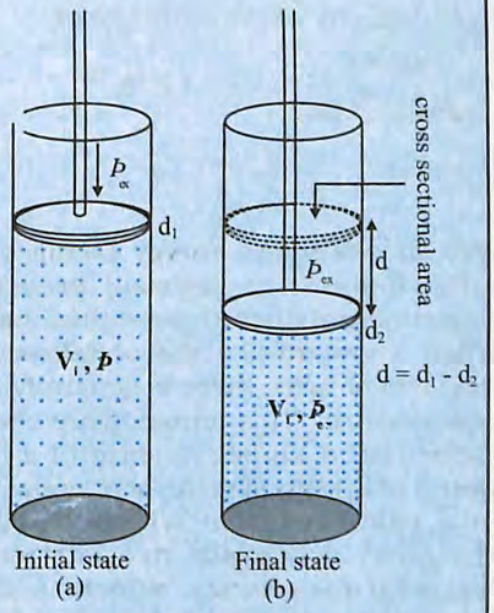


Fig.5.3

The negative sign of this expression is necessary to give the conventional sign for w which will be positive in case of compression as work is done on the system. Here $(V_f - V_i)$ will be negative and negative multiplied by negative will be positive.

5.3 HEAT CAPACITY AND SPECIFIC HEAT CAPACITY

The **heat capacity** (C) of a sample of a substance is the quantity of heat needed to raise its temperature by one degree celsius (or one kelvin). C_V is the heat capacity when the temperature is raised keeping volume constant while C_p is the heat capacity where pressure is kept constant during temperature rise. For solids and liquids, there is not much difference between the values of C_V and C_p , however, for gases these quantities differ. Changing the temperature of the sample from initial temperature t_i to a final temperature t_f requires heat equal to

$$q = C_V \Delta T \quad \text{where} \quad \Delta T = (t_f - t_i)$$

Suppose a piece of a metal requires 6.80 J of heat to raise the temperature by one degree celsius at constant volume. Then value for C_V is, therefore, 6.80 J/°C. The quantity of heat 'q' required to raise the temperature of the piece of metal from 20.0°C to 30.0°C is

$q = C_V \Delta T = (6.80\ J/°C) \times (30.0°C - 20.0°C)$

$= 68.0\ J$

Heat capacity is directly proportional to the amount of a substance.

In chemical calculations, we often use the terms **specific heat capacity and molar heat capacity.**

The *molar heat capacity* of a substance is its heat capacity for one mole of the substance. The *specific heat capacity, c,* is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). For finding out the heat, q required to raise the temperature of a sample, we multiply the specific heat capacity of the substance, c, by the mass *m*, and temperature change, ΔT.

$$q = c \times m \times \Delta T$$

Specific heat capacity of water is 4.18 J/(g K) and in terms of calories, it will be 1.00 cal/g K. *Specific heat capacity and molar heat capacity of a few substances are given in Appendix at the end of the book.*

In order to illustrate the calculation of specific heat capacity, let us take a suitable example. It has been found that 60.8 J are required to change the temperature of 25.0 g of ethylene

glycol (a compound used as an antifreeze in automobile engines) by 1.0 K. Therefore specific heat capacity of ethylene glycol

$$= \frac{60.8\text{J}}{(25.0\text{g})\ (1.0\text{K})} = 2.43\ \text{J g}^{-1}\text{K}^{-1}$$

5.4 MEASUREMENT OF ΔU AND ΔH : CALORIMETRY

We can determine energy changes associated with chemical or physical processes by an experimental technique called **calorimetry**. When a system absorbs or releases energy in the form of heat, there is generally a change in temperature. This temperature change can be measured. A known amount of a liquid (often water) of known specific heat capacity, is taken in a calorimeter in which the physical or chemical processes are carried out. The temperature change, which is due to heat released or absorbed during the process, is measured. Knowing the heat capacity of the liquid and the calorimeter, it is possible to determine the heat evolved in the process. Measurements of energy changes are made under two different conditions:

(i) at constant volume and

(ii) at constant pressure.

At constant volume,

$$\Delta U = q_v,$$

i.e., heat absorbed gives the increase in internal energy.

At constant pressure, heat absorbed is equal to increase in enthalpy, i.e,

$$\Delta H = q_p$$

Measurements at constant pressure are very common as many chemical and physical processes, including that in nature take place at constant pressure. For chemical reactions heat absorbed at constant volume, is measured in a **bomb calorimeter**. (Fig.5.4). A strong steel vessel (the bomb) is immersed in a large volume of water. A combustible sample is burned in pure oxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and only a small change in temperature occurs. In this measurement, oxygen and compound represent the system and bomb and water around it are the surroundings. In a bomb calorimeter, the energy changes associated with reactions are measured at *constant volume and almost constant temperature.* No work is done in this case as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$.

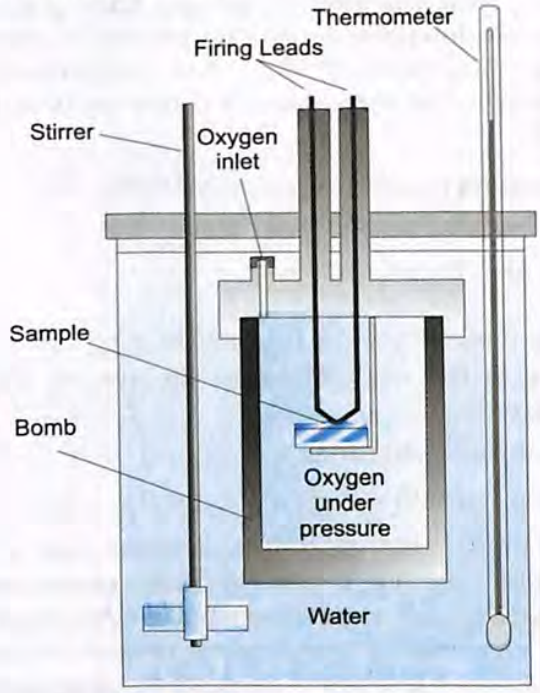


Fig 5.4 *Bomb calorimeter*

Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in Fig.5.5. We know $\Delta H = q_p$ (at constant p,T) and, therefore, heat absorbed, q_p at constant pressure is also called the *heat of reaction* or *enthalpy change*, ΔH. Here, we measure the heat absorbed in relation to initial temperature of the system.

In an *exothermic reaction* heat is evolved, and system loses heat to surroundings. Therefore, q_p will be negative and ΔH will also be negative. Similarly in an *endothermic reaction*, heat is absorbed, q_p is positive and ΔH will also be positive. In brief, *ΔH will be positive for endothermic reactions and negative for exothermic reactions.* In exothermic reactions, loss of energy shows that reactants were at higher level of enthalpy than the products. Similarly in *endothermic reactions*, the reactants are at lower level of enthalpy than the products. This is represented in Fig.5.6.

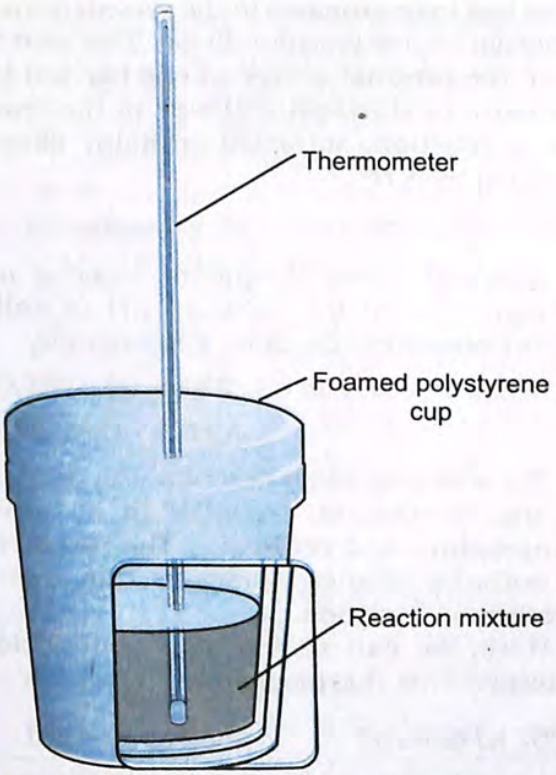


Fig.5.5 *Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).*

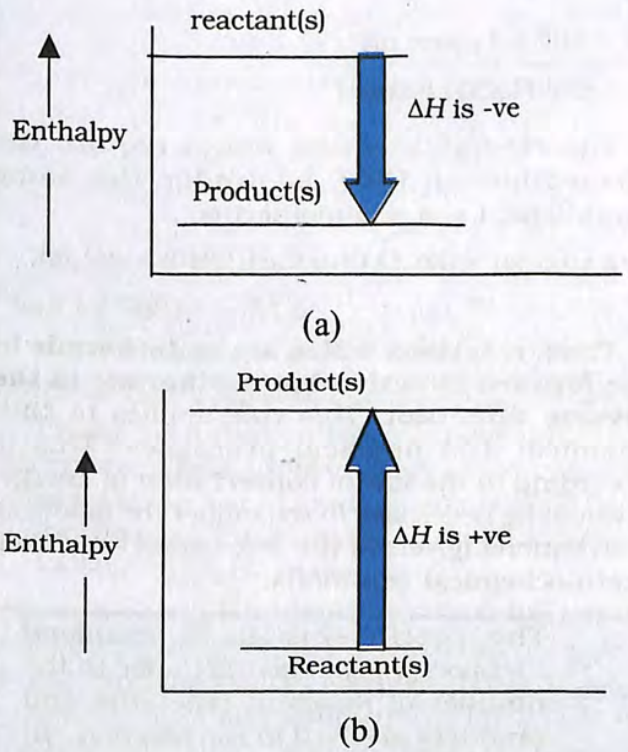


Fig 5.6 *Enthalpy diagram for (a) exothermic and (b) endothermic reactions.*

Example 5.1

0.562 g of graphite kept in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure was burnt according to the equation

$$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)$$

During the reaction, temperature rises from 298 K to 298.89 K. if the heat capacity of the calorimeter and its contents is 20.7 kJ/K, what is the enthalpy change for the above reaction at 298K and 1atm ?

Solution

Suppose q is the quantity of heat from the reaction mixture and C_v is the heat capacity of the calorimeter and the content, then the quantity of heat absorbed by the calorimeter

$$= C_v \times \Delta T$$

Quantity of heat from the reaction will have the same magnitude but opposite sign i.e.

$$q = C_v \times \Delta T = -20.7\ kJ/K \times (298.89 - 298)\ K$$
$$= -18.4\ kJ$$

(Here, negative sign indicates the exothermic nature of the reaction)

Thus, ΔH for the combustion of the 0.562 g of carbon = −18.4 kJ

For combustion of 1 mol of carbon, heat released

$$= 1\ mol\ C \times \frac{12.0g\ C}{1\ mol\ C} \times \frac{(-18.4\ kJ)}{0.562g\ C}$$

$= -3.9 \times 10^2$ kJ (result reported to two significant figures)

Thus, enthalpy for combustion of graphite

$= -3.9 \times 10^2\ kJ\ mol^{-1}$

Enthalpy change, ΔH of a reaction

Reactants → Products

is represented by

$\Delta_r H$ = (sum of enthalpies of products) − (sum of enthalpies of reactants)

$$= \Sigma H_{products} - \Sigma H_{reacants}$$

(Here symbol Σ (sigma) is used for summation).

5.5 STANDARD ENTHALPY CHANGES

Reaction enthalpies depend on the conditions under which a reaction is carried out. It is,

therefore, necessary that we must specify some standard condition. ***The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances (elements and compounds) are in their standard states.*** **The standard state of a substance at a specified temperature is its pure form at 1 bar**. For example, the standard state of liquid ethanol at 298K is pure liquid ethanol at 298K and 1 bar; standard state of solid iron at 500 K is pure iron at 500 K and 1 bar. Usually data are chosen at 298K. Mostly enthalpy changes in this book are provided at 298K. The standard enthalpy change for a reaction or for a physical process is the difference between enthalpy of the products in their standard states and enthalpy of the reactants in their standard states all at the same specified temperature.

Standard conditions are denoted by adding the superscript $\ominus$ to the symbol ΔH. For the combustion of 1 mol of methane under standard conditions, we write the equation

$$CH_4(g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)\ ;\quad \Delta_c H^\ominus = -890.4\ kJ\ mol^{-1}$$

Here subscript 'c' is used for combustion in standard states. If enthalpy change is measured at 298 K, we add 298 K and denote as $\Delta_c H^\ominus$ (298 K). The equation for combustion of methane indicates that in the combustion of 1 mol of CH_4 in sufficient oxygen or air, 1 mol of CO_2 and 2 mol of H_2O are formed and 890.4 kJ of heat is released at a pressure of 1 bar and at 298 K. It might seem surprising that the combustion can apparently be carried out at 298 K. In fact, when methane is ignited, its temperature rises rapidly as it burns and produces heat, so that combustion is in fact not occurring at 298 K. But if reactant(s) are at 298 K at the start of the reaction and products are at 298 K at the completion of the reaction, all the heat produced in the reaction is eventually transferred to the calorimeter during measurement. If the reactants are initially at 298 K and products formed also finally come to a temperature of 298 K, it is immaterial that during the reaction temperature is higher than 298 K. Similarly in an endothermic reaction, which is started with the reactants at 298 K and proceeds with an absorption of heat, the products are finally to be at 298 K, and as such heat has to be supplied to the system from some external source (surroundings). This heat taken from the external source at one bar will be the measure of standard enthalpy of the reaction. For a reaction, standard enthalpy change is denoted by $\Delta_r H^\ominus$.

5.6 THERMOCHEMICAL EQUATIONS

A balanced chemical equation together with a designation of its value of ΔH is called a thermochemical equation. For example,

$$C_2H_5OH\ (l) + 3O_2\ (g) \rightarrow 2\ CO_2\ (g) + 3H_2O\ (l)\ ;\quad \Delta_r H^\ominus = -1367\ kJ\ mol^{-1}$$

The above equation describes the combustion of liquid ethanol, C_2H_5OH (l) at constant temperature and pressure. The negative sign of enthalpy change indicates that this is an exothermic reaction.

Here, we can use several *unit factors* to interpret this thermochemical equation :

$$\frac{1367\ kJ\ given\ off}{mol\ of\ reaction} = \frac{1367\ kJ\ given\ off}{mol\ of\ C_2H_5OH(l)\ consumed} =$$

$$\frac{1367\ kJ\ given\ off}{3\ mol\ O_2(g)\ consumed} = \frac{1367\ kJ\ given\ off}{2\ mol\ CO_2(g)\ formed}$$

$$= \frac{1367\ kJ\ given\ off}{3\ mol\ H_2O(l)\ formed}$$

The reverse reaction would require the absorption of 1367 kJ under the same conditions, i.e. it is endothermic .

$$2\ CO_2\ (g) + 3H_2O\ (l) \rightarrow C_2H_5OH(l) + 3O_2(g);\quad \Delta_r H^\ominus = +1367\ kJ\ mol^{-1}$$

Thus, reactions which are endothermic in the forward direction are exothermic in the reverse direction. This rule applies to both chemical and physical processes. This is according to the law of conservation of energy. It would be necessary to remember the following conventions (given in the box below) regarding thermochemical equations.

1. The coefficients in a *balanced thermochemical equation* refer to the number of *moles* of reactants and products involved in the reaction. In the thermodynamic interpretation of an equation, we never interpret the

coefficients as *number of molecules*. Thus, it is acceptable to write coefficients as fractions rather than as integers, wherever necessary.

2. The numerical value of $\Delta_r H^\ominus$ refers to the number of moles of substances specified by an equation. Standard enthalpy change $\Delta_r H^\ominus$ is, therefore, expressed as enthalpy change as per moles shown in equation. In brief, the unit of $\Delta_r H^\ominus$ will remain kJ mol^{-1} even if more than one mole of a reactant or product are involved but its magnitude will change.
3. When a chemical equation is reversed, the value of ΔH is reversed in sign. For example

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \quad \Delta_r H^\ominus = -91.8 \text{ kJ mol}^{-1}$$

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g); \quad \Delta_r H^\ominus = +91.8 \text{ kJ mol}^{-1}$$

4. Physical states of all species is important and must be specified in a thermochemical equation as ΔH depends on the phase of the substances. For two states of water in following two equations, value of $\Delta_r H^\ominus$ is different.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g); \quad \Delta_r H^\ominus = -483.7 \text{ kJ mol}^{-1}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l); \quad \Delta_r H^\ominus = -571.1 \text{ kJ mol}^{-1}$$

5. The value of $\Delta_r H$ usually shows small change with increase of temperature (provided there are no phase changes when the temperature is increased).

If it is found that enthalpy change at 298 K during burning of 1 mol of CO(g) under constant pressure of one bar in a calorimeter is –283.0 kJ.

The thermochemical equation can be written as

$$CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g); \quad \Delta_r H^\ominus = -283.0 \text{ kJ mol}^{-1}$$

If the equation is multiplied throughout by 2, the enthalpy change also should be doubled and then we should write

$$2\left[CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g)\right]; \quad \Delta_r H^\ominus = 2 \times (-283.0 \text{ kJ mol}^{-1})$$

or $2CO(g) + O_2(g) \rightarrow 2\,CO_2(g)$; $\Delta_r H^\ominus = -566.0 \text{ kJ mol}^{-1}$

In both cases the units of $\Delta_r H^\ominus$ are kJ mol^{-1} as the multiplication is only by a number.

Example 5.2

Red phosphorus reacts with liquid bromine in an exothermic reaction,

$2\,P(s) + 3\,Br_2(l) \rightarrow 2\,PBr_3(g)$; $\Delta_r H^\ominus = -243 \text{ kJ mol}^{-1}$.

Calculate the enthalpy change when 2.63 g of phosphorus reacts with an excess of bromine in this way.

Solution

Molar mass of phosphorus = 30.97 g mol^{-1}

Amount of phosphorous

$$= \frac{m}{M} = \frac{2.63\text{g}}{30.97\text{g mol}^{-1}} = 0.0849 \text{ mol of P}$$

Here, enthalpy change of –243 kJ is associated with two moles of phosphorus, we can construct a *conversion factor* and use it to calculate the enthalpy change associated with 0.0849 mol as

$$\Delta H = 0.0849 \text{ mol P} \times \left(\frac{-243 \text{ kJ}}{2 \text{ mol P}}\right) = -10.3 \text{ kJ}$$

At constant pressure, 10.3 kJ of heat will be released for this amount (0.0849 mol) of phosphorus. The '2 mol P' appears in the denominator of the conversion factor because of the coefficient '2' with P in the balanced chemical equation.

5.6.1 Standard Enthalpy of Combustion

Combustion reactions are exothermic in nature. These are important in industry, rocketry, and other walks of life. **Standard enthalpy of combustion is defined as the enthalpy per mole (or per unit amount) of a substance, all the reactants and products being in their standard states at the specified temperature.**

Cooking gas in cylinders contains mostly butane (C_4H_{10}). During complete combustion of one mole of butane, 2658 kJ of heat is released.

$C_4H_{10}(g) + 13/2\ O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$;

$\Delta_c H^\ominus = -2658.0\ kJ\ mol^{-1}$

Similarly, combustion of glucose carried out in a bomb calorimeter gives out 2802 kJ/mol of heat.

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$;

$\Delta_c H^\ominus = -2802\ kJ\ mol^{-1}$

Our body also generates energy from food by the same overall process as combustion although the final products are produced after a series of complex bio-chemical reactions involving enzymes.

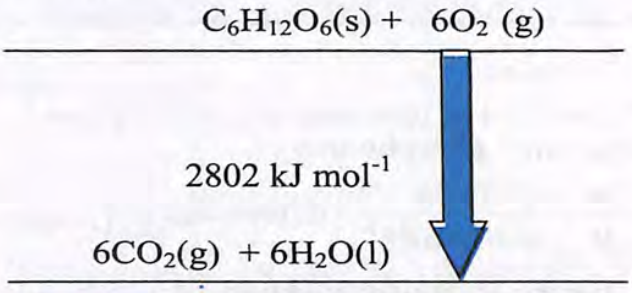


Fig.5.6a The combustion enthalpy of glucose

5.6.2 Enthalpy of Neutralization

When a solution of hydrochloric acid is added to a solution of sodium hydroxide both dissolved in water, heat is released. This is called enthalpy of neutralization and reaction is represented by

$HCl\ (aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) + Heat$

In the case of strong acids and bases (Unit 8), the net reaction is the formation of water from the reaction of hydrogen ions (H^+) with hydroxyl ions (OH^-).

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$;

$\Delta_n H^\ominus = -57.1\ kJ\ mol^{-1}$

Thus *neutralization enthalpy* is the enthalpy change per mole of H_2O that is formed on neutralization of an acid with a base. The value remains constant per mole of water formed for most strong acids and bases. (Neutralization enthalpies are usually quoted for the infinitely dilute solutions to avoid complication arising from interaction of ions).

The amount of energy released in general also depends on the nature of the acids and bases and this helps in identification of nature of acids and bases i.e. whether they are strong or weak. (You will learn more about acids and bases and their weak and strong nature in Unit 8). In case of neutralization of a weak acid with a strong base or vice versa, enthalpy of neutralization will be less than 57.1 kJ mol^{-1} as some energy will be used in dissociating acid or base molecules.

5.7 ENTHALPY CHANGES DURING PHASE TRANSFORMATIONS

Phase changes also involve energy changes. Ice, for example, requires heat for melting. Normally this melting takes place at constant pressure (atmospheric pressure) and during phase change, temperature remains constant (at 273K).

$H_2O(s) \rightarrow H_2O(l)$; $\Delta_{fus} H^\ominus = 6.00\ kJ\ mol^{-1}$

Here $\Delta_{fus}H^\ominus$ is *enthalpy of fusion in standard state.* If water freezes, then process is reversed and an equal amount of heat is given off to the surroundings, that is

$\Delta_{freez} H^\ominus = -\Delta_{fus} H^\ominus$

The enthalpy change that accompanies melting per mole of a solid substance is called enthalpy of fusion or ***molar enthalpy of fusion.*** $\Delta_{fus}H^\ominus$ *of the substance*

$\Delta_{fus} H^\ominus = H^\ominus_{liquid} - H^\ominus_{solid}$

Melting of a solid is endothermic, so all enthalpies of fusion are positive.

Standard enthalpy changes of fusion and vaporization for some substances are given in Table 5.1.

Amount of heat required to vaporize one mole of a liquid at constant pressure and temperature is called its enthalpy of vaporization or molar enthalpy of vaporization. Here constant temperature is its boiling point, T_b. In case of water vaporization.

$H_2O(l) \rightarrow H_2O(g)$; $\Delta_{vap} H^\ominus = +40.79\ kJ\ mol^{-1}$

Molar enthalpy of vaporization, fusion and sublimation are also characteristic properties of substances. Sublimation is direct conversion of a solid into its vapour. Solid CO_2 or *'dry ice'* sublimes at 195 K with $\Delta_{sub}H^\ominus = 25.2\ kJ\ mol^{-1}$, naphthalene sublimes slowly and for this $\Delta_{sub}H^\ominus = 73.0\ kJ\ mol^{-1}$.

Because enthalpy is a state property, the enthalpy of sublimation can be expressed as

$\Delta_{sub}H^{\ominus} = \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus}$ (see Fig. 5.7)

For example, at 298K, enthalpy of fusion of sodium metal is +2.6 kJmol^{-1} and enthalpy of vaporization of liquid sodium is + 98.0 kJmol^{-1}. Therefore, enthalpy of sublimation of solid sodium at 298K is written as

$\Delta_{sub}H^{\ominus} = \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus}$

= 2.6 kJ mol^{-1} + 98.0 kJ mol^{-1} = 100.6 kJ mol^{-1}

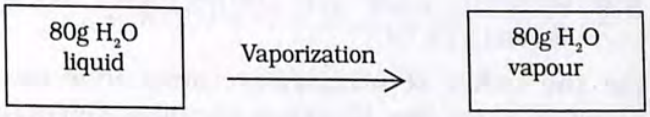
The magnitude of the enthalpy change depends on the strength of the intermolecular interaction in the substances undergoing the phase changes. For example, intermolecular hydrogen bonds between water molecules lead to large attractive intermolecular energy holding water molecules tightly in liquid phase. For an organic liquid, such as acetone, the intermolecular dipole-dipole interactions are significantly weaker. Thus it requires less heat to vaporize 1 mole of acetone than it does to vaporize 1 mole of water (Table 5.1).

Example 5.3

A swimmer coming out from a pool is covered with a film of water weighing about 80 g. How much heat must be supplied to evaporate this water (use Table 5.1).

Solution

We can represent the process of evaporation as



$\Delta_{vap}H^{\ominus}$ for water is 40.79 kJmol^{-1} and the molar mass of water is 18.0 g mol^{-1}.

80g of water is, $\frac{80g}{18.0g\ mol^{-1}} = 4.44$ mol

Therefore, heat that must be supplied is as follows:

$q_p = n\,\Delta_{vap}H^{\ominus} = (4.44\ mol)\ (40.79\ kJmol^{-1})$

$= 1.81 \times 10^2$ kJ

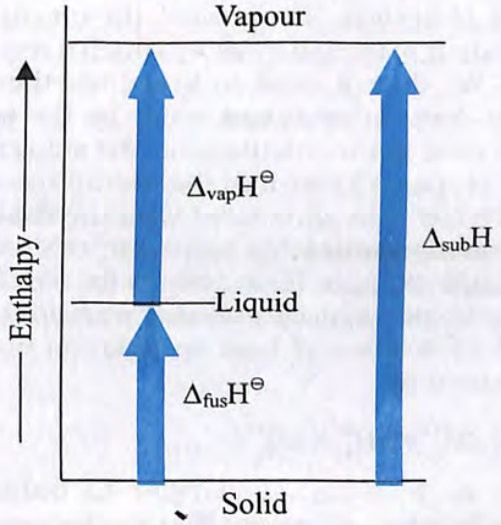


Fig.5.7 *Enthalpy of sublimation can be expressed as the sum of the enthalpies of fusion and vaporisation.*

Table 5.1 Standard Enthalpy Changes of Fusion and Vaporization

Substance	T_f/K	$\Delta_{fus}H^{\ominus}$/(kJ mol^{-1})	T_b/K	$\Delta_{vap}H^{\ominus}$/(kJ mol^{-1})
N_2	63.15	0.72	77.35	5.59
NH_3	195.40	5.65	239.73	23.35
HCl	159.0	1.992	188.0	16.15
CO	68.0	6.836	82.0	6.04
CH_3COCH_3	177.8	5.72	329.4	29.1
CCl_4	250.16	2.5	349.69	30.0
H_2O	273.15	6.01	373.15	40.79
NaCl	1081.0	28.8	1665.0	170.0
C_6H_6	278.65	9.83	353.25	30.8

(T_f and T_b are melting and boiling points, respectively)

5.8 HESS'S LAW OF CONSTANT HEAT SUMMATION

On the basis of numerous thermochemical observations, the Russian chemist Germain Henri Hess (a professor at the University of St. Peterburg) in 1840, stated this law which goes by his name as **Hess's Law of Constant Heat Summation.** The law states that **if a reaction is the sum of two or more constituent reactions, then ΔH for the overall process must be sum of the ΔH's of the constituent reactions**. In brief, **the enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps.** This is consistent with the fact that enthalpy is a state function. Therefore, its change is independent of the pathway by which a reaction occurs. We do not need to know whether the reaction does, or even **can** occur by the series of steps used in the calculation. The steps must (if only 'on paper') result in the overall reaction.

Hess's law is in agreement with the **first law of thermodynamics**. It helped in calculation of enthalpy changes for reactions for which the changes could be measured only with difficulty, if at all. Hess's law of heat summation may be represented as

$$\Delta_r H^\ominus = \Delta H_a^\ominus + \Delta H_b^\ominus + \Delta H_c^\ominus + \ldots\ldots\ldots$$

Here a, b, c .....refer to balanced thermochemical equations that can be summed to give the equation for the desired reaction.

Let us consider the following reaction :

$$C_{(graphite)} + \tfrac{1}{2} O_2(g) \rightarrow CO(g) \; ; \; \Delta_r H^\ominus = ?$$

We cannot measure enthalpy change for this reaction directly. Although CO(g) is the predominant product of the reaction of graphite with limited amount of O_2(g) but some CO_2 is always produced. However, the following reactions do go to completion with excess O_2(g). Therefore, $\Delta_r H^\ominus$ values have been measured experimentally for them

$$C_{(graphite)} + O_2(g) \rightarrow CO_2(g) \; ;$$
$$\Delta_r H^\ominus = -393.5 \text{ kJ/mol} \quad \text{(a)}$$

$$CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g) \; ;$$
$$\Delta_r H^\ominus = -283.0 \text{ kJ/mol} \quad \text{(b)}$$

Here we have to combine these two reactions in such a way that we obtain the desired reaction. We want one mole of CO on the right, so we reverse equation (b). In this, heat is absorbed instead of being released and for this we must change the sign of its $\Delta_r H^\ominus$ value. Equation (c) obtained in this way is added to equation (a), cancelling equal numbers of moles of the same species on each side we get the equation for the reaction we want (see Fig. 5.8).

$$C_{(graphite)} + O_2(g) \rightarrow \cancel{CO_2}(g) \; ;$$
$$\Delta_r H^\ominus = -393.5 \text{ kJ mol}^{-1} \quad \text{(a)}$$

$$\cancel{CO_2}(g) \rightarrow CO(g) + \tfrac{1}{2} O_2(g) ;$$
$$\Delta_r H^\ominus = -(-283.0 \text{ kJ mol}^{-1}) \quad \text{(c)}$$

$$C_{(graphite)} + \tfrac{1}{2} O_2(g) \rightarrow CO(g) \; ;$$
$$\Delta_r H^\ominus = -110.5 \text{ kJ mol}^{-1}$$

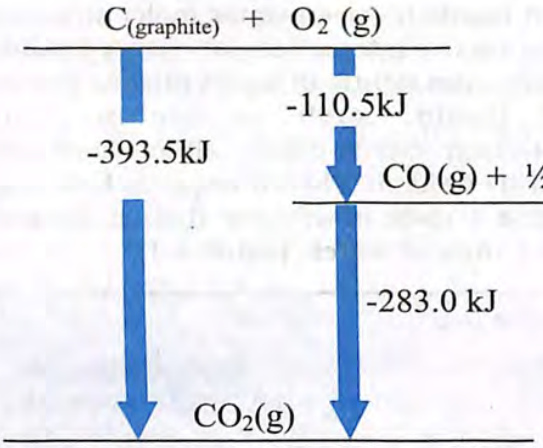


Fig.5.8 *A schematic representation of enthalpy changes for the reaction $C_{(graphite)} + \tfrac{1}{2} O_2(g) \rightarrow CO(g)$. The $\Delta_r H^\ominus$ value for each step refers to the number of moles of each substance indicated).*

Example 5.4

With the help of thermochemical equations given below, determine $\Delta_r H^\ominus$ at 298 K for the following reaction.

$$C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g) \; ; \; \Delta_r H^\ominus = ?$$

$$C_{(graphite)} + O_2(g) \rightarrow CO_2(g) \; ;$$
$$\Delta_r H^\ominus = -393.5 \text{ kJ mol}^{-1} \quad (1)$$

$$H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l) \; ;$$
$$\Delta_r H^\ominus = -285.8 \text{ kJ mol}^{-1} \quad (2)$$

$$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g) ;$$
$$\Delta_r H^\ominus = +890.3 \text{ kJ mol}^{-1} \quad (3)$$

Solution

Here we want one mole of $C_{(graphite)}$ as reactant, so we write down equation (1), we want two mole of $H_2(g)$ as reactant, so we multiply equation (2) by 2, we want one mole of $CH_4(g)$ as product, so we write down equation (3) as such.

$C_{(graphite)} + O_2(g) \rightarrow CO_2(g)$;

$\Delta_r H^\ominus = -393.5$ kJ/mol (1)

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$;

$\Delta_r H^\ominus = 2(-285.8$ kJ/mol) (2)

$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$;

$\Delta_r H^\ominus = +890.3$ kJ/mol (3)

Adding we obtain

$C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g)$;

$\Delta_r H^\ominus = -74.8$ kJ mol^{-1}

5.9 STANDARD ENTHALPIES OF FORMATION

A formation reaction is one that produces 1 mol of a substance from the elements in their most stable forms at 1 bar at any specified temperature. For example,

$$Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$$

$$C_{graphite} + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$$

Here each one, mercuric chloride and methyl alcohol, are formed from the constituent elements.

The standard enthalpy change for the formation of one mole of a compound from its elements in their standard states is called Standard Molar Enthalpy of formation, $\Delta_f H^\ominus$, where the subscript of 'f' indicates that one mole of the compound in question has been formed in its standard state from its elements in their standard states. Some reactions with standard molar enthalpies of formation are given below.

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$;

$\Delta_f H^\ominus = -285.8$ kJ mol^{-1}

$2C_{graphite} + 2H_2(g) \rightarrow C_2H_4(g)$;

$\Delta_f H^\ominus = 52.26$ kJ mol^{-1}

Similarly graphite (the standard state for carbon) when combines with gaseous hydrogen and oxygen at 1 bar and forms one mole of ethyl alcohol at 298K, we have

$2C_{(graphite)} + 3H_2(g) + \frac{1}{2} O_2(g) \rightarrow C_2H_5OH(l)$;

$\Delta_f H^\ominus = -277.7$ kJ mol^{-1}

It is important to understand that a *standard molar enthalpy of formation*, $\Delta_f H^\ominus$, is just a special case of $\Delta_r H^\ominus$, the case where one mole of a compound is formed from its elements, as in the above three equations where 1 mole of each: water, ethane and ethanol is formed. In contrast, the enthalpy change for an exothermic reaction

$CaO(g) + CO_2(g) \rightarrow CaCO_3(s)$;

$\Delta_r H^\ominus = -178.3$ kJ mol^{-1}

is not an enthalpy of formation of calcium carbonate. Since calcium carbonate has been formed from other compounds, not from its elements. For the reaction given below,enthalpy change is also not standard enthalpy of formation, $\Delta_f H^\ominus$ for HBr(g).

$H_2(g) + Br_2(l) \rightarrow 2HBr(g)$; $\Delta_r H^\ominus = -72.8$ kJ mol^{-1}

Here two moles instead of one mole of the product is formed from the elements, $\Delta_r H^\ominus = 2\Delta_f H^\ominus$.

Therefore, by dividing all coefficients in the balanced equation by 2, we get

$\Delta_f H^\ominus = -36.4$ kJ mol^{-1}.

Hence, expression for enthalpy of formation of HBr(g) is written as

$\frac{1}{2} H_2(g) + \frac{1}{2} Br_2(l) \rightarrow HBr(g)$; $\Delta_f H^\ominus = -36.4$ kJ mol^{-1}

Standard enthalpy of formation of some common substances are given in Table 5.2.

By convention, standard enthalpy for formation, $\Delta_f H^\ominus$, of an element in its standard state is taken as zero. Suppose you are a chemical engineer and want to know how much heat is required to decompose calcium carbonate to lime and carbon dioxide, with all the substances in their standard state.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$; $\Delta_r H^\ominus = ?$

Here, we can make use of standard enthalpy of formation and calculate the enthalpy change for the reaction. The following general equation can be used for the enthalpy change calculation.

$\Delta_r H^\ominus = \Sigma[a\, \Delta_f H^\ominus \text{ (products)}] - \Sigma[b\, \Delta_f H^\ominus \text{ (reactants)}]$

where a and b represent the coefficients in the balanced equation. Let us apply the above equation for decomposition of calcium carbonate. Here, coefficients 'a' and 'b' are 1.

Table 5.2 Standard Molar Enthalpies of Formation ($\Delta_f H^\ominus$) at 298K of a Few Selected Substances

Substance	$\Delta_f H$ / (kJ mol^{-1})	Substance	$\Delta_f H$ /(kJ mol^{-1})
Al_2O_3(s)	-1675.7	HI(g)	+26.48
$BaCO_3$(s)	-1216.3	KCl(s)	-436.74
Br_2(l)	0	KBr(s)	-393.8
Br_2(g)	+30.91	MgO(s)	-601.70
$CaCO_3$(s)	-1206.92	$Mg(OH)_2$(s)	-924.54
C (diamond)	+1.89	NaF(s)	-573.65
C (graphite)	0	NaCl(s)	-411.15
CaO(s)	- 635.09	NaBr(s)	-361.06
CH_4(g)	-74.81	NaI(s)	-287.78
C_2H_4(g)	52.26	NH_3(g)	-46.11
CH_3OH(l)	-238.66	NO(g)	+ 90.25
C_2H_5OH(l)	-277.69	NO_2(g)	+33.18
C_6H_6(l)	+ 49.03	PCl_3(l)	-319.70
CO(g)	-110.525	PCl_5(s)	-443.5
CO_2(g)	-393.51	SiO_2(s) (quartz)	-910.94
C_2H_6(g)	-84.68	$SnCl_2$(s)	-325.1
Cl_2(g)	0	$SnCl_4$(l)	-511.3
C_3H_8(g)	-103.2	SO_2(g)	-296.83
n– C_4H_{10}(g)	-888.0	SO_3(g)	-395.72
HgS(s) red	-58.2	SiH_4(g)	+34
H_2(g)	0	$SiCl_4$(g)	-657.0
H_2O(g)	-241.82	C(g)	+715.0
H_2O(l)	-285.83	H(g)	+218.0
HF(g)	-271.1	Cl(g)	+121.3
HCl(g)	-92.30		
HBr(g)	-36.40		

Therefore,

$\Delta_r H^\ominus = a\Delta_f H^\ominus$ [CaO(s)] + $a\Delta_f H^\ominus$[CO_2)(g)] – $b\Delta_f H^\ominus$ [$CaCO_3$(s)]

= 1(–635.1 kJ mol^{-1}) + 1(–293.5 kJ mol^{-1} –1(–1206.9 kJ mol^{-1})

= 178.3 kJ mol^{-1}

Thus, decomposition of $CaCO_3$(s) is endothermic and you have to heat it for getting the desired products.

Example 5.5

The combustion of one mole of benzene takes place at 298K and 1atm. After combustion, CO_2(g) and H_2O(l) are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^\ominus$ of benzene.

Solution

Combustion of 1 mol of benzene takes place as follows

C_6H_6(l) + 7 ½ O_2 (g) → 6CO_2(g) + 3H_2O(l)

$\Delta_c H^\ominus$ = -3267.0 kJ mol^{-1}

$\Delta_r H^\ominus = \Delta_c H^\ominus = \Sigma[a\Delta_f H^\ominus$(products)] - $\Sigma[b\Delta_f H^\ominus$ (reactants)]

or –3267.0 kJ mol^{-1} = 6($\Delta_f H^\ominus$ (CO_2(g)) + 3($\Delta_f H^\ominus$(H_2O(l)) – 1($\Delta_f H^\ominus$(C_6H_6(l)) –7 ½ ($\Delta_f H^\ominus$ (O_2(g))

Using the Table 5.2,

–3267 kJ mol^{-1} = (6) (–393.5 kJ mol^{-1}) + (3)(–285.83 kJ mol^{-1}) – (1)($\Delta_f H^\ominus$ (C_6H_6(l)) – 0

or $\Delta_f H^\ominus$ C_6H_6(l) = [6 (–393.5) + 3 (–285.83) + 3267] kJ mol^{-1}

= [–2361.0 – 857.49 + 3267.0] kJ mol^{-1}

$= 48.51 \text{ kJ mol}^{-1}$

5.10 BOND ENTHALPIES

Chemical reactions involve the breaking and making of chemical bonds. Energy is required to break a bond and energy is released when a bond is formed. (It is possible to relate heat of reaction to changes in energy associated with breaking and formation of chemical bonds). Strictly speaking, we should use ΔU for this purpose. One of the important contributions of thermochemistry to physical chemistry is that it provides bond enthalpies and enthalpy of formation of atoms. The bond enthalpy for the reaction at 298.15 K

$$H_2(g) \rightarrow 2H(g) \; ; \; \Delta_a H^\ominus = 435.0 \text{ kJ mol}^{-1}$$

The corresponding bond energy $\Delta_a U^\ominus$ for the same reaction is 430.8 kJ mol^{-1}. Thus it can be seen that there is very small difference between the two quantities and very often these are used interchangeably. As a matter of fact, bond dissociation energy is obtained at 0 K by spectroscopic methods and $\Delta_a H^\ominus$ and $\Delta H^\ominus$ at any other temperatures are calculated by considering contributions from heat capacities and $p\Delta V$ terms.

The bond enthalpies are very important quantities as reaction enthalpy arises from the changes that accompany the breaking of old bond and formation of the new ones. We can predict enthalpy for a reaction in gas phase if we know different bond enthalpies.

The bond enthalpy is the amount of energy necessary to break bonds in one mole of a gaseous covalent substance to form products in the gaseous state.

As mentioned above the bond enthalpy for H_2 is 435.0 kJ mol^{-1}.

This endothermic reaction (as $\Delta_a H^\ominus$ is positive) can also be written as

$$H_2(g) + 435 \text{ kJ} \rightarrow 2H(g)$$

Bond energy of a diatomic molecule (e.g. H_2,Cl_2,O_2 etc.) is equal to its **dissociation energy. The dissociation energy of a bond is defined as enthalpy change involved in breaking the bond between atoms of a gaseous homonuclear molecule.**

It can be seen that bond enthalpy in the above reaction is twice the enthalpy of formation for hydrogen atom in the gaseous state. The values of some bond energies are given in Table 5.3.

Let us now consider a polyatomic molecule like methane, CH_4. The overall thermochemical equation for its atomization reaction is given below:

$$CH_4(g) \rightarrow C(g)+4H(g); \; \Delta_a H^\ominus = 1.66 \times 10^3 \text{ kJ mol}^{-1}$$

In methane all the four hydrogen atoms are identical, therefore, C–H bonds are also identical in *bond length* and *energy* in a methane molecule. However, the energies required to break the individual C – H bonds in steps differ for each successive bond, as shown below.

$$CH_4(g) \rightarrow CH_3(g) + H(g); \; \Delta_r H^\ominus = + 427 \text{ kJ mol}^{-1}$$
$$CH_3(g) \rightarrow CH_2(g) + H(g); \; \Delta_r H^\ominus = + 439 \text{ kJ mol}^{-1}$$
$$CH_2(g) \rightarrow CH(g) + H(g); \; \Delta_r H^\ominus = + 452 \text{ kJ mol}^{-1}$$
$$CH(g) \rightarrow C(g) + H(g); \; \Delta_r H^\ominus = + 347 \text{ kJ mol}^{-1}$$

Therefore,

$$CH_4(g) \rightarrow C(g) + 4H(g), \; \Delta_a H^\ominus = 1665 \text{ kJ mol}^{-1}$$

We now define the *'average'* bond enthalpy of C–H bond in

$$CH_4 = \tfrac{1}{4} (\Delta_a H^\ominus) = \tfrac{1}{4} (1665 \text{Kj mol}^{-1})$$

$$416 \text{ kJ mol}^{-1}$$

We find that average C – H bond enthalpy in methane is 416 kJ/mol. It has been found that average C–H bond enthalpies differ slightly from compound to compound, as in CH_3CH_2Cl, CH_3NO_2 etc. but it does not differ a great deal. Using Hess's law bond enthalpies can be calculated and a table of bond enthalpy is available. A special case of Hess's law involves the use of bond enthalpies to estimate enthalpies of reactions (Fig.5.9). The Standard Enthalpy of reaction, $\Delta_r H^\ominus$ is related to bond energies of the reactants and products in gas phase reactions by the following relationship.

$$\Delta_r H^\ominus = \Sigma \text{bond enthalpies}_{\text{reactants}} - \Sigma \text{bond enthalpies}_{\text{products}}$$

This relationship is particularly more useful when the required values of $\Delta_f H^\ominus$ are not available. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in the reactant molecules minus the amount of energy required to break all the bonds in the product molecules. Please remember that *this relationship is approximate and is valid when all*

Table 5.3(a) Some Average Single Bond Enthalpies in kJ mol^{-1} of Bonds

H	C	N	O	F	Si	P	S	Cl	Br	I	
436	414	389	464	569	293	318	339	431	368	297	H
	347	293	351	439	289	264	259	330	276	238	C
		159	201	272	–	209	–	201	243?	–	N
			138	184	368	351	–	205	–	201	O
				159	540	490	327	255	197?	–	F
					176	213	226	360	289	213	Si
						213	230	331	272	213	P
							213	251	213	–	S
								243	218	209	Cl
									192	180	Br
										151	I

Table 5.3(b) Some Average Multiple Bond Enthalpies in kJ mol^{-1}

N = N	418	C = C	611	O = O	498
N ≡ N	946	C ≡ C	837		
C = N	615	C = O	741		
C ≡ N	891	C ≡ O	1070		

substances (reactants and products) in the reaction are in gaseous state.

Example 5.6

Use the bond enthalpies listed in Table 5.3(a) to estimate the enthalpy change for the reaction, $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

Solution

We have seen above

$$\Delta_r H^\ominus = \Sigma \text{bond enthalpies}_{\text{reactants}} - \Sigma \text{bond enthalpies}_{\text{products}}$$

$$= \left[H^\ominus_{H-H} + H^\ominus_{Br-Br}\right] - 2\left[H^\ominus_{H-Br}\right]$$

$$= (435 \text{ kJ mol}^{-1} + 192 \text{ kJ mol}^{-1}) - (2 \times 368 \text{ kJ mol}^{-1})$$

$$= 627 \text{ mol}^{-1} - 736 \text{ kJmol}^{-1} = -109 \text{ kJ mol}^{-1}$$

A schematic representation of the relationship is given in Fig.5.9. Different kinds of standard enthalpy changes are summarized in Table 5.4.

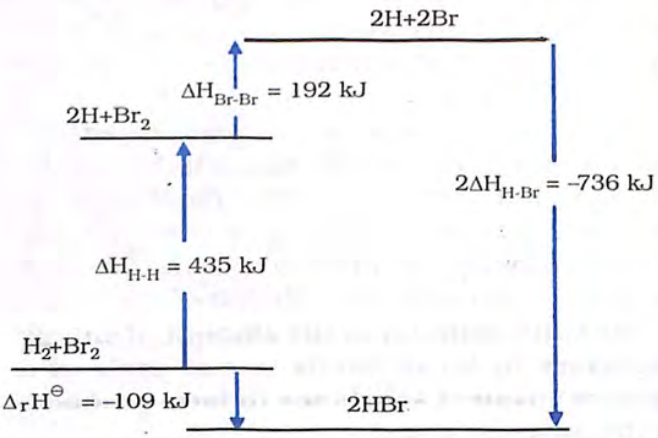


Fig 5.9 *A schematic representation of the relationship between bond enthalpies (energies) for the gas phase reaction, $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$.*

5.11 SOURCES OF ENERGY

5.11.1 Conventional and Alternative Sources of Energy

We have noted in the preceding section that combustion of fuel produces heat energy that is used in running vehicles, producing electricity, cooking food and for many other activities. Generally the **fossil fuels** like coal, petroleum products and natural gas are used for this purpose, and these are called conventional fuels. Progress in generation of energy from nuclear, hydro and wind resources has been made in India still more than 90% of the total energy consumed is derived from fossil fuels. Primary energy consumption pattern of India and the world is shown in Fig. 5.10. The

Table 5.4 Some Examples of Special Kind of Standard Enthalpy Changes

Name	Symbol	Description of process to which enthalpy applies	Example of process
Enthalpy of formation	$\Delta_f H^\ominus$	One mole of compound formed from its elements	$Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$
Enthalpy of Combustion	$\Delta_c H^\ominus$	One mole of a fuel burned in oxygen	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
Enthalpy of neutralization	$\Delta_n H^\ominus$	One mole of water formed by the neutralization of an acid by a base	$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$
Ionization Enthalpy	$\Delta_I H^\ominus$	One mole atoms ionized: all species in the gas phase	$K(g) \rightarrow K^+(g) + e^-$ (first ionization enthalpy)
Electron gain enthalpy (- Δ_{eg} H ≈ electron affinity)	$\Delta_{eg} H^\ominus$	One mole of anions being formed - all species in the gas phase	$Cl(g) + e^- \rightarrow Cl^-(g)$
Lattice enthalpy	$\Delta_L H^\ominus$	One mole of a crystal completely separated into isolated particles in the gas phase	$K^+Cl^-(s) \rightarrow K^+(g) + Cl^-(g)$
Bond dissociation enthalpy (of a specific bond A – B)	$\Delta H^\ominus_{(A-B)}$	One mole of bonds broken: all species in the gas phase	$HCl(g) \rightarrow H(g) + Cl(g)$
Enthalpy of atomization	$\Delta_a H^\ominus$	One mole of substance broken up into its isolated atoms in the gas phase	$Na(s) \rightarrow Na(g)$
Enthalpy of fusion	$\Delta_{fus} H^\ominus$	One mole of a liquid being formed from the solid without a change in temperature	$H_2O(s) \rightarrow H_2O(l)$
Enthalpy of vaporization	$\Delta_{vap} H^\ominus$	One mole of vapour formed from the liquid without a change in temperature	$H_2O(l) \rightarrow H_2O(g)$

sudden spurt in the petroleum prices affected by the oil producing countries in mid 2000, threw out of gear the economic activities in the countries across the world which are dependent heavily on imported petroleum and petroleum products. At the same time, there has been threat from global warming, rising sea levels and climate change due to increasing atmospheric pollution caused by green house gas emissions from economic activities based on fossil fuels. All these have only strengthened the view that the process of economic development cannot be sustained for long by relying on fossil fuels. This is all the more true in the light of projection that with the present rate of consumption, the world will run out of conventional fuel ere long. There is, thus, an increasing realization, that switch over to **alternative sources** (non-conventional and renewable sources) to meet the growing energy needs of a burgeoning population cannot be delayed any further. Spurred by environmental concerns, the developed countries even have stepped up efforts to increase the share of renewables in meeting their energy requirements.

In order to increase the tempo of work in this direction India has an exclusive Ministry for Non-conventional Energy Sources (MNES). In 1950, Indian scientists thought of using solar energy for cooking and water heating. The devices they developed were technologically sound but in the then prevalent scenario of cheap oil, they were not found economically viable as compared to conventional system based on fossil fuels. However, the subsequent oil shock in the 1970s and the increasing environmental concerns led to a revival of interest in those devices. Consequently the

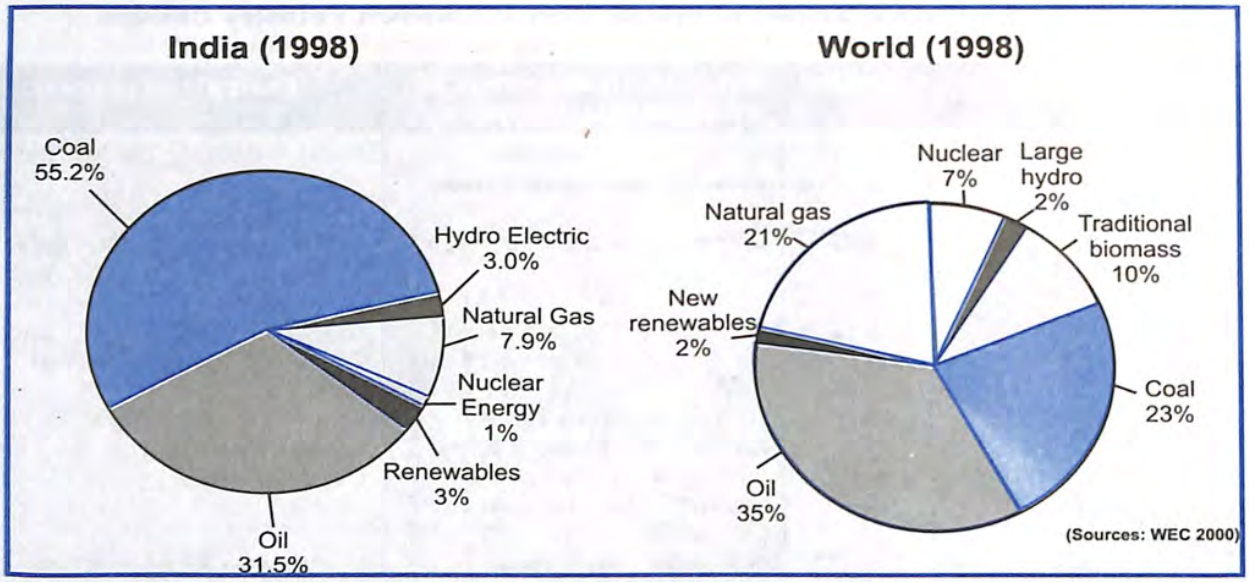


Fig.5.10

contribution of renewable energy to the total installed capacity of power generation has been progressively rising. As on Dec. 31,2000, the contribution of renewable energy sources has reached 3000 MW representing 3 percent of total grid capacity. Nearly all sources like solar, wind, biomass, industrial wastes and small hydro project have been tapped for this purpose. The potential and achievements in respect of various New and Renewable sources of Energy (NRSE) devices are given Table 5.5.

5.11.2 Sun as a primary source of Energy

Sun is the ultimate source of energy and this is clear from the Fig.5.11. The formation of elements is believed to have occurred stepwise from hydrogen by the process of nuclear fusion occurring in stars (Unit 10). In that sense,

Table 5.5 Renewable Energy Potential and Achievements Under Various Programmes of Non-conventional Energy Sources as on 31st August 2001 in India

S. No	Source/System	Approximate Potential	Achievement
1.	Biogas plants (No.)	12.0 million	3.22 million
2.	Improved Chulha (No.)	120 million	33.861 million
3.	a. Biomass Power	19,500 MW	343 MW
	b. Biomass Gasifier		41.00 MW
4.	Solar Photovoltaic	20 MW/ km^2	
	i. Solar Street Lighting Systems	-	41,403
	ii. Home Lighting Systems	-	159,000
	iii. Solar Lanterns	-	368,000
	iv. SPV Power Plants	-	1,132 kWp
5.	Solar Water Heating Systems	30 million m^2 Collector area	590,000 m^2 collector area
6.	Solar Cookers		510,000
7.	Solar PV Pumps		4,204
8.	Solar Photovoltaic Power		1.74 MW
9.	Wind Power	45,000 MW	1,367 MW
10.	Small Hydro Power (upto 25 MW)	15,000 MW	1,398 MW
11.	Wind Pumps		714
12.	Hybrid Systems		101.5 kW
13.	Energy Recovery from wastes	1,700 MW	16.2 MW
14.	Battery Operated Vehicles No.		240

(kWp = Kilo watt peak)

everything that we see around, including ourselves and the heaviest element uranium we use as nuclear fuel, are all children of stardust. Hence, stars in general (and our sun in particular) are the ultimate source of all our energy.

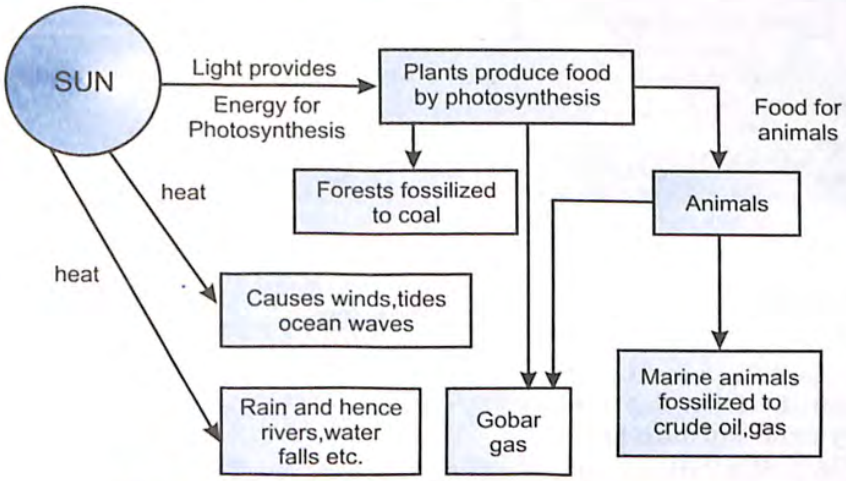


Fig.5.11 Sun as a primary source of energy

SUMMARY

Thermodynamics plays a central role in chemistry because energy changes are very important in chemical reactions. Chemical processes lead to evolution of heat (q), part of which may be converted into work (w). These quantities are related through the first law of thermodynamics, $\Delta U = q + w$. Both heat and work depend on the way the change occurs and, thus, are not function of state. It is important to understand that we can observe only the *transfer* of heat from one place to another. A heat transfer causes temperature change whose magnitude depends on the heat capacity (C) of the substance:

$q = nC\Delta T$. This relationship between heat flow and temperature change is the working equation for the **calorimetric measurements**. Work results when a force generates a displacement. Work of expansion against a constant external pressure is given by $w = p_{ex}\Delta V_{system}$. When volume of a system remains fixed, no expansion work occurs. Under these conditions, heat absorbed and energy change are equal: $\Delta U = q_v$. The enthalpy change also does not depend on the path we choose to follow and therefore enthalpy, H is a state function. In most of the chemical processes, pressure is constant, but volume is not and for these processes enthalpy is a useful function. Enthalpy is defined as $H = U + pV$. At constant pressure, the change in enthalpy can be found directly from the heat flow : $\Delta H = q_p$.

For many chemical reactions not involving gases, enthalpy change (ΔH) and internal energy change (ΔU) differ so little that these can be used interchangeably.

Changes of phase such as melting, vaporization and sublimation usually occur at constant temperature and can be characterized by their enthalpy changes. The enthalpy changes of fusion, vaporization, and sublimation are always positive. Solution enthalpies, which involve a balance between solid phase cohesion and solute – solvent attraction, may be positive or negative. The chemical equation including $\Delta_r H$ is referred to as the **thermochemical equation**. We can use these equations to calculate the heat for any amount of substance by applying stoichiometry of the reaction. Hess's law provides an important method for calculating enthalpy changes.

It states that, if a reaction is the sum of two or more reactions, then ΔH for overall process is the sum of the ΔH's of the constituent reactions. Enthalpy change for chemical processes can be determined using **molar enthalpies of formation**.

$$\Delta_r H^\ominus = \sum[a\Delta_f H^\ominus(\text{product})] - \sum[b\Delta_f H^\ominus(\text{reactants})]$$

Enthalpy changes of a chemical reaction in gaseous state can also be estimated using bond energy data.

$$\Delta_r H^\ominus = \sum \text{bond enthalpies of the reactants} - \sum \text{bond enthalpies of the products}$$

EXERCISES

5.1 Explain the following terms:
(a) System, surroundings
(b) State function
(c) Heat capacity, molar heat capacity

5.2 Define the following terms:
(a) Standard enthalpy of formation
(b) Bond enthalpy
(c) Zeroth law of Thermodynamics
(d) Reversible and irreversible process

5.3 In what way internal energy is different from enthalpy? Explain both the terms with suitable examples.

5.4 Which of following are open, close or nearly isolated systems? (i) Human being, (ii) the earth, (iii) Can of tomato soup, (iv) Ice-cube tray filled with water, (v) A satellite in an orbit, (vi) Coffee in a thermos flask, and (vii) Helium filled balloon.

5.5 Which of the following are state functions?
(i) height of a hill
(ii) distance travelled in climbing the hill
(iii) energy change in climbing the hill

5.6 Give the appropriate reason for the followings:
(i) It is preferable to determine a change in enthalpy than change in internal energy.
(ii) It is necessary to define the 'Standard State'.
(iii) It is necessary to specify the phases of the reactants and products in a thermochemical equation.

5.7 (a) Calculate the energy needed to raise the temperature of 10.0 g of iron from 25^0C to 500^0C if specific heat capacity of iron is 0.45 J $(^0C)^{-1}$ g^{-1}.
(b) What mass of gold (of specific heat capacity 0.13 J $(^0C)^{-1}$ g^{-1} can be heated through the same temperature difference when supplied with the same amount of energy as in (a)?

5.8 Standard vaporization enthalpy of benzene at its boiling point is 30.8 kJ mol^{-1}; for how long would a 100 W electric heater have to operate in order to vaporize a 100g sample of benzene at its boiling temperature? $\left(\text{power} = \frac{\text{energy}}{\text{time}},\ 1W = 1Js^{-1}\right)$

5.9 Use the standard enthalpies of formation (Table 5.2) and calculate the enthalpy changes accompanying the following reactions:
(a) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
(b) $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

5.10 Acetic acid (ethanoic acid) and hydrochloric acid react with KOH solution. The enthalpy of neutralisation of ethanoic acid is – 55.8 kJ mol^{-1} while that of hydrochloric acid is –57.3 kJ mol^{-1}. Can you think of how are these different?

5.11 Specific heat of Li(s), Na(s), K(s), Rb(s) and Cs(s) at 398 K are 3.57, 1.23, 0.756, 0.363, and 0.242 $Jg^{-1}K^{-1}$, respectively. Compute the molar heat capacity of these elements and identify any periodic trend. If there is trend, use it to predict the molar heat capacity of Fr.

5.12 Calculate the enthalpy change when 2.38g of carbon monoxide (CO) vaporize at its normal boiling point. (Use the data given in the Table 5.1).

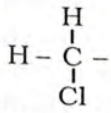
5.13 Propane has the structure $H_3C - CH_2 - CH_3$. Use the average bond enthalpies from the Table 5.3a to estimate the change in enthalpy, ΔH, for the following reaction:
$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

5.14 In the above reaction (problem 5.13), if standard enthalpy change $\Delta_r H^{\ominus} = -2.05 \times 10^3$ kJ / mol and bond energies of C–C, C–H, C = O and O–H remains the same as given in the Table 5.3a., calculate the energy of oxygen – oxygen bond in O_2 molecules and compare the calculated value with the value given in the table.

5.15 What is the basic difference between enthalpy of formation and enthalpy of reaction? Illustrate with suitable examples.

5.16 Use standard enthalpies of formation to calculate the value of $\Delta_r H^{\theta}$ for the reaction $2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2SO_2(g)$. ($\Delta_f H^{\ominus}_{H_2S} = -20.15$ kJ mol^{-1})

5.17 Calculate the $\Delta_r H^{\ominus}$ for the reaction



(Use table for standard enthalpy of formation).

5.18 The enthalpy change (ΔH) for the reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is –92.38 kJ at 298 K. What is ΔU at 298 K?

5.19 A 1.250g sample of octane (C_8H_{18}) is burned in excess of oxygen in a bomb calorimeter. The temperature of calorimeter rises from 294.05 K to 300.78 K. If heat capacity of the calorimeter is 8.93 kJ/K, find the heat transferred to calorimeter.

5.20 20.0 g of ammonium nitrate (NH_4NO_3) is dissolved in 125 g of water in a coffee- cup calorimeter, the temperature falls from 296.5 K to 286.4 K. Find the value of q for the calorimeter. (Hint: Treat heat capacity of water as the heat capacity of the calorimeter and its content).

5.21 A chemist while studying the properties of gaseous $C_2Cl_2F_2$, a chlorofluoro carbon refrigerant, cooled a 1.25 g sample at constant atmospheric pressure of 1.0 atm from 320 K to 293 K. During cooling, the sample volume decreased from 274 to 248 mL. Calculate ΔH and ΔU for the chlorofluoro carbon for this process. For $C_2Cl_2F_2$, C_p = 80.7 J/(mol K).

5.22 Compounds with carbon – carbon double bond, such as ethylene, C_2H_4, add hydrogen in a reaction called hydrogenation,
$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
Calculate enthalpy change for the reaction, using the following combustion data
$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$; $\Delta_c H^{\ominus} = -1401$ kJ mol^{-1}
$C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta_c H^{\ominus} = -1550$ kJ mol^{-1}
$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$; $\Delta_c H^{\ominus} = -286.0$ kJ mol^{-1}.

UNIT 6

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Objectives

After studying this Unit, you will be able to

- know about Kossel- Lewis approach to chemical bonding, the octet rule, its limitations and Lewis representations of simple molecules.
- understand ionic bond, lattice enthalpy and Born-Haber cycle.
- understand the meaning of covalent bond, bond length, bond enthalpy, bond order, resonance, electronegativity and polarity of bonds.
- describe the VSEPR model and predict the geometry of simple molecules.
- explain the valence bond approach,directional properties of bonds and hybridization of atomic orbitals.

"———They (the electrons) serve as the bonds of union between atom and atom"

Why do atoms of the same element or different elements combine – to form compounds? What are the forces which hold atoms together in molecules in different arrangements? Why particular shapes are adopted by molecules. What particular arrangements of ions in ionic compounds are preferred? These are some of the basic questions to which we will seek answers in this unit.

We already know that a molecule is a group of atoms having a distinct existence and its own characteristic properties. Molecules may be **homonuclear diatomic like: H_2, O_2, Cl_2; heteronuclear diatomic like CO, HF, HCl, NO or homonuclear/heteronuclear polyatomic like P_4, S_8/ H_2O, NH_3, CO_2.** There are also a large number of compounds in which discrete molecules are not present, instead they are made up of ions/atoms arranged in characteristic three-dimensional patterns. Such compounds can be both ionic or covalent.

The tendency of elements to combine with one another is directly related to valency or valence of the element. The earliest definition of valency as the ability or power of elements to combine with one another is too qualitative and simplistic. Obviously what is required, for logical understanding, is a quantitative definition of valence.

The evolution of various theories of valence and the interpretation of the nature of chemical bonds have closely been related to the developments in the understanding of the structure of atom, the electronic configuration of elements and the periodic table. **The elucidation of the structure of hydrogen atom provided the first firm foundation for the systematic development of a theory of valence.** The independent research publications of **W.Kossel** and **G.N.Lewis** in 1916, were the two most important initial contributions in

this context. Over the years further refinements of their ideas in the light of experimental and theoretical advances have produced the **VSEPR** theory, the **Valence Bond** theory and the **Molecular Orbital** theory to explain chemical bonding and molecular structure.

Gilbert Newton Lewis (1875-1946) is considered to be one of the top physical chemists of the twentieth century. He made important contributions in the areas of chemical bonding, thermodynamics, acids and bases, and spectroscopy. Paradoxically, he was not awarded the Nobel Prize in chemistry.

6.1 KOSSEL-LEWIS APPROACH TO CHEMICAL BONDING

W.Kossel, in relation to chemical bonding, drew attention to the facts, that :

- In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases;
- The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms;
- The negative and positive ions so formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet) electrons, ns^2np^6.
- The negative and positive ions are stabilized by electrostatic attraction.

For example, the formation of NaCl from sodium and chlorine, according to the above scheme, can be explained as:

Na	⟶	$Na^+ + e^-$
[Ne] $3s^1$		[Ne]
$Cl + e^-$	⟶	Cl^-
[Ne] $3s^2\ 3p^5$		[Ne] $3s^2\ 3p^6$ or [Ar]
$Na^+ + Cl^-$	⟶	NaCl or $Na^+\ Cl^-$

Similarly the formation of $Ca\ F_2$ may be shown as:

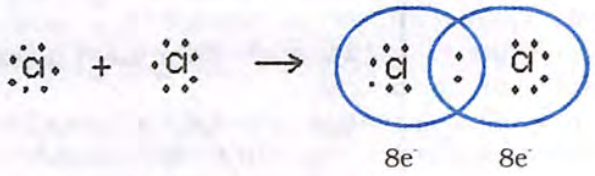
Ca	⟶	$Ca^{2+} + 2e^-$
[Ar]$4s^2$		[Ar]
$F + e^-$	⟶	F^-
[He] $2s^2\ 2p^5$		[He] $2s^2\ 2p^6$ or [Ne]
$Ca^{2+} + 2F^-$	⟶	CaF_2 or $Ca^{2+}.\ 2F^-$

The link formed, as a result of the electrostatic attraction between the positive and negative ions was termed, the electrovalent bond. The electrovalency being equal to the number of unit charges on the ion. Thus calcium is assigned a positive electrovalency of two, while chlorine a negative electrovalency of one.

Kossel's postulations provide the basis for the modern concepts regarding ion-formation by electron transfer and the formation of ionic crystalline compounds. His views have proved to be of great value in the understanding and systematization of the ionic compounds. At the same time he did recognise the fact that a large number of compounds did not fit into his concepts.

Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell that could accommodate a maximum of eight electrons. He, further assumed that these eight electrons occupy the corners of a cube which surrounds the 'Kernel'. Thus the single outer shell electron of sodium would occupy one corner of the cube, while in the case of a noble gas all the eight corners would be occupied. This octet of electrons, represents a particularly stable electronic arrangement. **Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.** In the case of sodium and chlorine, this can happen by the transfer of an electron from sodium to chlorine thereby giving the Na^+ and Cl^- ions. In the case of other molecules like Cl_2, H_2, F_2, etc., the bond is formed by the sharing of a pair of electrons between the atoms. In the process each atom attains a **stable outer octet of electrons**. Each of the combining atoms contributes one electron to the electron pair. **Langmuir** (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet and by introducing the term **covalent bond**. The Lewis-Langmuir theory can be understood by considering, as an example, the formation of the chlorine molecule, Cl_2. The Cl atom with electronic configuration, [Ne]$3s^2\ 3p^5$, is one electron short of the argon configuration, [Ne] $3s^2\ 3p^6$. The formation of the Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms. Each

chlorine atom contributing one electron to the shared pair. In the process both chlorine atoms attain the outer shell octet of a noble gas (in this case that of argon).



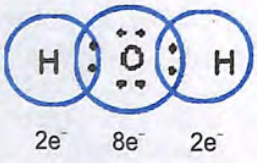
or Cl —— Cl

Covalent bond between two Cl atoms

The dots represent electrons. Such structures are referred to as Lewis dot structures.

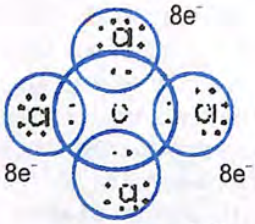
The Lewis dot structures can be written for other molecules also, in which the combining atoms may be alike or different. The important conditions being that :

- Each bond is formed as a result of sharing of an electron pair between the atoms.
- Each combining atom contributes one electron to the shared pair.
- The combining atoms attain the outer-shell noble gas configurations as a result of the sharing of electrons.
- Thus in the water and carbon tetrachloride molecules the formation of bonds can be represented as:



H_2O

The H atom attains a duplet of electrons , He configuration



8e⁻ CCl_4

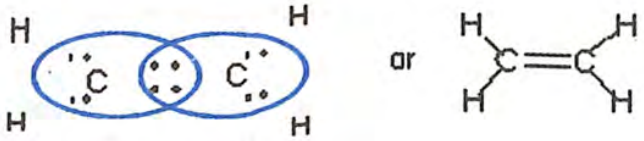
Each of the four Cl atoms along with the C atom attains octet of electrons.

The two atoms joined by one electron pair are said to be joined by a single covalent bond. In many compounds we have **multiple bonds** between atoms. The formation of multiple bonds envisages sharing of more than one electron pair between two atoms. **If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.** For example, in the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms and in the ethene molecule the two carbon atoms are joined by a double bond.

When two combining atoms share three electron pairs as in the case of two nitrogen atoms in the N_2 molecule and the two carbon atoms in the ethyne molecule a triple bond is formed.

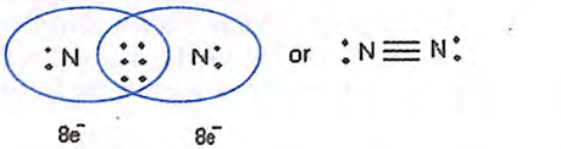
8e⁻ 8e⁻ 8e⁻

CO_2 molecule



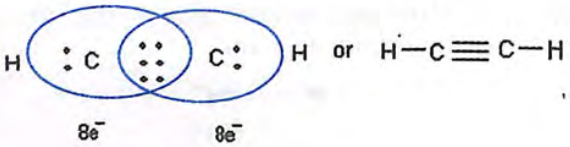
8e⁻ 8e⁻

C_2H_4 molecule



8e⁻ 8e⁻

N_2 molecule

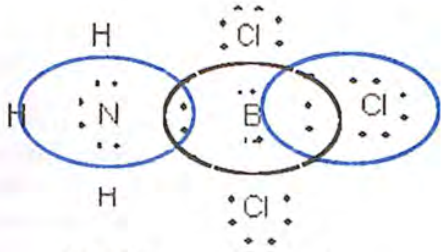


8e⁻ 8e⁻

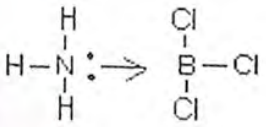
C_2H_2 molecule

Perkins (1921), postulated a related type of bond formation in which the electron pair used for sharing is donated solely by one of the combining atoms. For example, in the combination of ammonia, NH_3, with boron trichloride, BCl_3, the available electron pair on the nitrogen atom in ammonia is donated to boron of BCl_3 which accepts it resulting in the formation of a bond between NH_3 and BCl_3. The structure satisfies

the octet rule for B, N and Cl atoms. Alternatively, the process of donation of the electron pair by one atom and its acceptance by the other atom is represented as *electronic charge displacement*, resulting in the formation of a **dipolar molecule**.



$8e^-$ (N) $8e^-$ (Cl^-)

or 

The arrow indicates donor-acceptor relationship

Thus, the nitrogen atom in NH_3BCl_3 would acquire a formal positive charge and the boron atom a formal negative charge, $H_3N^+ B^-Cl_3$. **This type of bond has been variously named as: semi-polar, coordinate, dative, co-ionic or donor-acceptor bond. In the modern terminology, there is no distinction between a covalent and a coordinate bond. The bond formed is indistinguishable from a normal covalent bond because all electrons are alike irrespective of their source.** The distinction, however is useful to the extent that it helps in keeping track of valence electrons and for assigning formal charges. (See section 6.1.1)

6.1.1 Lewis Representation of Simple Molecules (the Lewis Structures)

The Lewis dot structures provide a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule. While such a picture may not explain the bonding and behaviour of a molecule completely, it does help in understanding the formation and properties of the molecule to a large extent. Writing of Lewis dot structures of molecules is, therefore, very useful. The Lewis-dot-structures can be written by adopting the following basic steps:

- The total number of electrons required for writing the structures are obtained by adding the valence electrons of the combining atoms. For example, in the CH_4 molecule there are eight valence electrons available for bonding (4 from carbon and 4 from the four hydrogen atoms).
- For anions, each negative charge would mean addition of one electron to and for cations, each positive charge would result in subtraction of one electron from the total number of valence electrons. For example, for the CO_3^{2-} ion we add two electrons, because the two negative charges indicate that there are two additional electrons than are provided by the neutral atoms. For NH_4^+ ion we subtract one electron because the 1+ charge indicates the loss of one electron from the group of neutral atoms.
- Knowing the chemical symbols of the combining atoms and having knowledge of the skeletal structure (what atoms are bonded to what other atoms) of the compound (known or guessed intelligently), it is easy to distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.
- In general the least electronegative atom occupies the central position in the molecule. Hydrogen and fluorine usually occupy the terminal positions, for example in the NF_3 and CO_3^{2-}, nitrogen and carbon respectively are the central atoms.
- After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are utilized either for multiple bonding or they constitute, the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.

The above mentioned procedure for writing of Lewis dot structures is illustrated by the following examples :

Example 6.1

Writing the Lewis dot structure of CO molecule

Solution

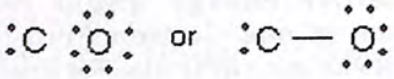
Step 1. Counting the total number of valence electrons of carbon and oxygen atoms.

The outer (valence) shell configurations of

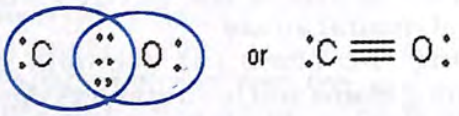
carbon and oxygen atoms are: $2s^2\ 2p^2$ and $2s^2\ 2p^4$ respectively. The valence electrons available are 4 + 6 =10.

Step 2. The skeletal structure of CO is written as: C O

Step 3. Drawing of a single bond (one shared electron pair) between C and O and completing the octet on O, the remaining two electrons are the lone pair on C.



This does not complete the octet on carbon and hence we have to resort to multiple bonding (in this case a triple bond) between C and O atoms. This satisfies the octet rule condition for both atoms.



Example 6.2

Writing the Lewis structure of the nitrite ion, NO_2^-.

Solution

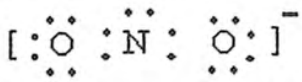
Step 1. Counting the total number of valence electrons of the nitrogen, the oxygen atoms and the additional one negative charge (equal to one electron).

N($2s^2\ 2p^3$), O ($2s^2\ 2p^4$)

5 + (2 x 6) +1 = 18 electrons

Step 2. The skeletal structure of NO_2^- is written as : O N O

Step 3. Drawing of a single bond (one shared electron pair) between the nitrogen and each of the oxygen atoms and completing the octets on oxygen atoms does not complete the octet on nitrogen if the remaining two electrons constitute lone pair on it.



Hence we have to resort to multiple bonding between nitrogen and one of the oxygen atoms (in this case a double bond) This leads to the following Lewis dot structures.

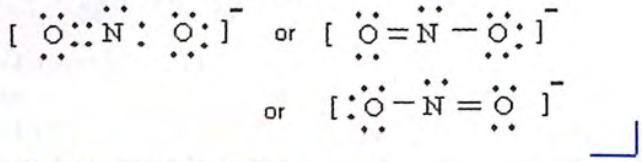
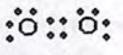
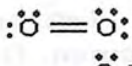
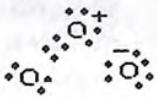
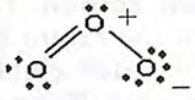
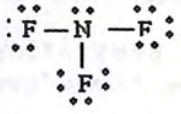
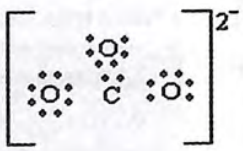
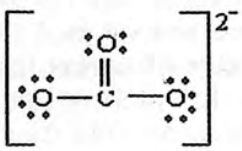
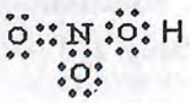
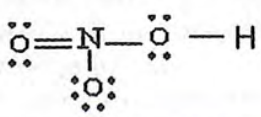


Table 6.1 The Lewis representations of some molecules and ions

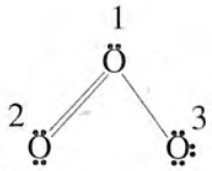
Molecule/Ion	Lewis Representation	
H_2	H : H *	H – H
O_2		
O_3		
NF_3		
CO_3^{2-}		
HNO_3		

* *Each H atom attains the configuration of helium (a duplet of electron)*

Lewis dot structures, in general, do not represent the actual shapes of the molecules. Although in the case of polyatomic ions the net charge is possessed by the ion as a whole and not by a particular atom, for some purposes a **Formal charge (F.C) is assigned to each atom. The formal charge of an atom in a polyatomic ion/molecule is defined as :**

Formal charge (F.C) On an atom in a Lewis structure = total number of valence electrons in the free atom − total number of non bonding (lone pair) electrons − ½ total number of bonding (shared electrons)

The formal charge is the difference between the number of valence electrons in an isolated (i.e. free) atom and the number of electrons assigned to that atom, in a Lewis structure. The counting being based on the assumption, that the atom in the molecule owns one electron of each shared pair and both the electrons of a lone pair. **The concept of formal charge can be illustrated by the ozone molecule, O_3.** Experimental data shows that in O_3, the central O atom is bonded to two other O atoms in the arrangement shown below :



Using the relationship given above, we can calculate the formal charges on the O atoms as follows:

- **The central O atom marked 1**

The central atom marked 1 has 6 valence electrons, one lone pair (or two non-bonding electrons) and three bonds (or six bonding electrons). Therefore its formal charge

$$= 6 - 2 - \frac{1}{2}(6) = +1$$

- **The end O atom marked 2**

This atom has 6 valence electrons, two lone pair (or 4 non-bonding electrons) and two bonds (or 4 bonding electrons). Therefore its formal charge

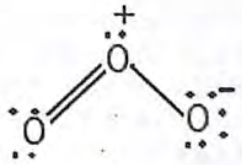
$$= 6 - 4 - \frac{1}{2}(4) = 0$$

- **The end O atom marked 3**

This atom has 6 valence electrons, three lone-pairs (or six non-bonding electrons) and one bond (or two bonding electrons). Thus its formal

$$\text{charge} = 6 - 6 - \frac{1}{2}(2) = -1$$

Therefore the formal charges on the oxygen atoms in the Lewis structures of O_3 given above are written as :



We must understand that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. **Generally the lowest energy structure is the one, with the smallest formal charges on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighboring atoms.**

6.1.2 Limitations of the Octet rule

The octet rule, though useful, is not universal. It is quite useful, for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

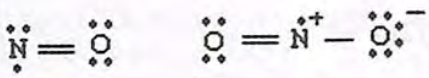
- **The Incomplete octet of the central atom**

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and BCl_3 .

Li, Be and B have 1,2 and 3 valence electrons only. Other such compounds are $AlCl_3$ and BF_3.

• Odd-Electron Molecules

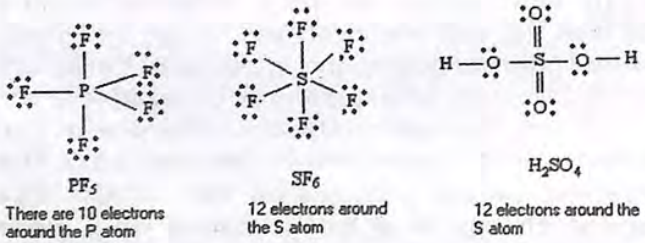
In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, the octet rule is not satisfied for all the atoms



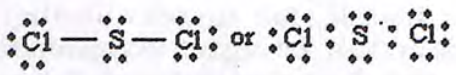
• The Expanded Octet

Elements in and beyond the third period of the periodic table have, apart from 3*s* and 3*p* orbitals, 3*d* orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF_5, SF_6, H_2SO_4 and a number of coordination compounds.



Interestingly sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride the S atom has an octet of electrons around it.



In next higher class you will be learning about the participation of *d*-orbitals in chemical bonding along with the *s* and *p* orbitals. Hybridizations of *s*, *p* and d orbitals like sp^3d and sp^3d^2 are invoked to explain the formation of PF_5 and SF_6 respectively.

• Other drawbacks of the octet theory

(i) it cannot account for the shape of a molecule; and (ii) it is totally silent about the energy of a molecule, that is about its relative stability.

The Kossel and Lewis approaches to chemical bonding as discussed in this section, provide the basis of a more detailed study of the ionic and covalent bonds given in the subsequent sections (6.2 and 6.3).

6.2 THE IONIC BOND

From the Kossel and Lewis treatment of the formation of an ionic bond (Section 6.1), it follows that the formation of ionic compounds would primarily depend upon.

- The ease of formation of the positive and negative ions from the respective neutral atoms; and,
- The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound.

The formation of a positive ion involves ionization, i.e., removal of electron (s) from the neutral atom and that of the negative ion involves the addition of electron(s) to the neutral atom.

$M(g) \longrightarrow M^+(g) + e^-$; Ionization enthalpy

$X(g) + e^- \longrightarrow X^-(g)$; Electron gain enthalpy

$M^+(g) + X^-(g) \longrightarrow MX(s)$

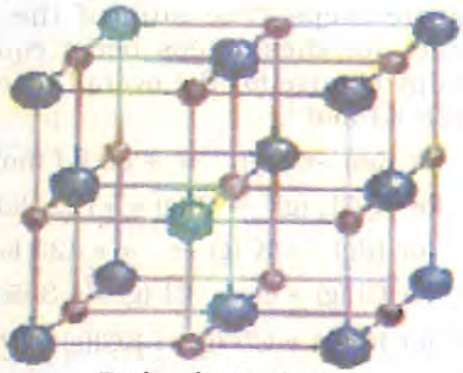
The **electron gain enthalpy, $\Delta_{eg}H$,** is the enthalpy change (unit 5), when a gas phase atom gains an electron. The electron gain process may be exothermic or endothermic. The ionization, on the other hand, is always endothermic. Electron affinity, is the negative of the energy change accompanying electron gain.

Obviously ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively low electron gain enthalpy.

Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two non-metallic elements) is an exception. It forms the cation of a number of ionic compounds.

Ionic compounds in the crystalline state consist of orderly three-dimensional arrangements of cations and anions held together by coulombic interaction energies. These compounds crystallize in different crystal structures determined by the size of the ions, their packing arrangements and other factors. The crystal structure of sodium

chloride, NaCl (rock salt), for example is shown below once again.



Rock salt structure

In ionic solids, the sum of the electron gain enthalpy and the ionization enthalpy may be positive but still the crystal structure gets stabilized due to the energy released in the formation of the crystal lattice. This energy as explained below is negative of the enthalpy of lattice formation. For example: the ionization enthalpy for Na^+ formation from Na is 495.8 kJ mol^{-1} ; while the electron gain enthalpy for the change $Cl(g) + e^-(g) \rightarrow Cl^-(g)$ is, –348.7 kJ mol^{-1} only. The sum of the two 147.1 kJ mol^{-1} is more than compensated for by the enthalpy of lattice formation of NaCl which is equal to 788 kJ mol^{-1}. **Thus a qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation.**

Since lattice enthalpy plays a key role in the formation of ionic compounds, it is important that we learn more about it.

6.2.1 Lattice Enthalpy (Lattice energy)

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example the lattice enthalpy of NaCl is 788 kJ mol^{-1}. This means that 788 kJ of energy is required to separate to an infinite distance 1 mol of solid NaCl into 1 mol of Na^+ (g) and one mole of Cl^-(g).

This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three-dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only. Factors associated with the crystal geometry have to be included.

The first theoretical interpretation of lattice enthalpy was given by Born and Lande. They gave a simple equation for the calculation of lattice enthalpy.

$$U_o = \frac{AN_A|z^+||z^-|e^2}{4\pi\varepsilon_o r_o}(1-1/n)$$

Where U_o is the lattice enthalpy; A, the Madelung constant; (this takes care of interaction with all the other ions besides the nearest neighbours) N_A, the Avogadro constant; z^+, charge on the positive ion; z^-, the charge on the negative ion; e, charge on the electron; π, constant (3.14159); ε_o, vacuum permittivity; r_o inter-ionic distance; n, the Born exponent in the repulsive terms. Other variables like van der Waals forces, zero-point energy and heat capacity are included for more accurate calculations. A detailed discussion of the above and other equations is beyond the scope of this book.

6.2.2 The Born–Haber Cycle

Determination of Lattice Enthalpy

We have already learnt that the direct calculation of lattice enthalpy is quite difficult because the required data is often not available. Therefore lattice enthalpy is determined indirectly by the use of the Born-Haber cycle. This cycle developed by Born and Haber, uses ionization enthalpies, electron gain enthalpies and other data for the calculation of lattice enthalpies. The procedure is based on the **Hess's law,** (Unit 5) which states that the enthalpy of a reaction is the same, whether it takes place in a single step or in more than one step. The assumption is that the formation of an ionic compound may occur either by direct combination

of the elements or by a stepwise process involving vaporization of elements, conversion of the gaseous atoms into ions and the combination of the gaseous ions to form the ionic solid.

The calculation of the lattice enthalpy, using the Born-Haber cycle, can be illustrated for a simple ionic solid such as an alkali metal halide, MX. A schematic representation is shown in Fig.6.1.

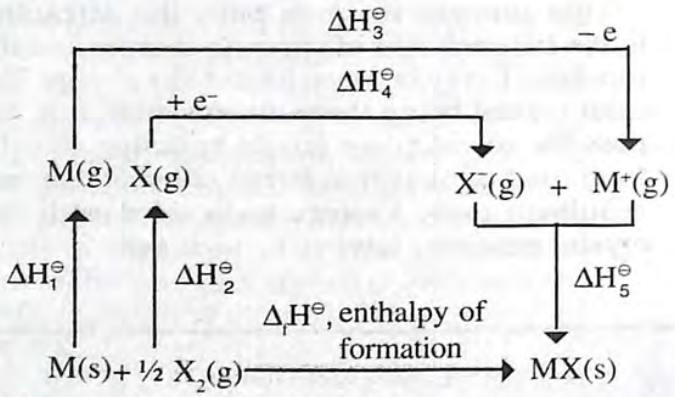


Fig.6.1 *A schematic representation of Born-Haber cycle for the formation of solid MX*

[Where $\Delta H^\ominus{}_1$, $\Delta H^\ominus{}_2$, $\Delta H^\ominus{}_3$, $\Delta H^\ominus{}_4$, and $\Delta H^\ominus{}_5$ are enthalpy changes for: sublimation of M(s) to M(g); dissociation of ½ X_2 (g) to X(g) ; ionization of M(g) to M^+(g) ; electron gain by X(g) to X^-(g) and lattice formation from M^+(g) and X^-(g) to MX(s). $\Delta_f H^\ominus$ overall = $\Delta H^\ominus{}_1 + \Delta H^\ominus{}_2 + \Delta H^\ominus{}_3 + \Delta H^\ominus{}_4 + \Delta H^\ominus{}_5$].

Example 6.3

Calculation of lattice enthalpy of KCl

Solution

Let us use the Born-Haber cycle for determining the lattice enthalpy of KCl.

The standard enthalpy change, $\Delta_f H^\ominus$ overall for the reaction,

K (s) + ½ Cl_2 (g) → KCl (s) is – 438 kJ mol^{-1}

Since the reaction is carried out with the reactants and products in their standard states (at 1 bar); the enthalpy change is also the standard enthalpy of formation for KCl. Here, the formation of KCl can be envisaged in five separate steps. The sum of the enthalpy changes for these steps being equal to the enthalpy change for the overall reaction, that is –438 kJ mol^{-1}.

$\Delta H_1^\ominus$ for K(s) → K(g) = + 89 kJ mol^{-1}

$\Delta H_2^\ominus$ for ½ Cl_2 (g) → Cl(g) = +122 kJ mol^{-1}

$\Delta H_3^\ominus$ for K(g) → K^+(g) + e^- = + 425 kJ mol^{-1}

$\Delta H_4^\ominus$ for Cl (g) + e^- → Cl^-(g) = – 355 kJ mol^{-1}

$\Delta H_5^\ominus$ for K^+ (g) + Cl^- (g) → KCl(s) = ?

The reverse of above equation , i.e., KCl(s) → K^+(g) + Cl^- (g) defines the lattice enthalpy of KCl.

Thus the lattice enthalpy is equal to $\Delta H_5^\ominus$ but with reverse sign. According to Hess's law we have:

$\Delta H^\ominus$ (overall) = $\Delta H^\ominus{}_1 + \Delta H^\ominus{}_2 + \Delta H^\ominus{}_3 + \Delta H^\ominus{}_4 + \Delta H^\ominus{}_5$

that is $-438 = +89 + 122 + 425 - 355 + \Delta H_5$

$\Delta H^\ominus{}_5$ = -719 kJ mol^{-1}

Hence the Lattice enthalpy of KCl = 719 kJ mol^{-1}.

Example 6.4

Calculation of lattice enthalpy of $MgBr_2$ from the given data.

Solution

The enthalpy of formation of Mg Br_2 according to the reaction

Mg(s) + Br_2 (l) → Mg Br_2 (s);

$\Delta_f H^\ominus$= -524 kJ/mol^{-1}

$\Delta H_1^\ominus$ for Mg(s) → Mg (g) = + 148 kJmol^{-1}

$\Delta H_2^\ominus$ for Mg(g) → Mg^{2+}(g) + $2e^-$ = +2187 kJmol^{-1}

$\Delta H_3^\ominus$ for Br_2(l) → Br_2 (g) = 31 kJmol^{-1}

$\Delta H_4^\ominus$ for Br_2(g) → 2Br(g) = 193 kJmol^{-1}

$\Delta H_5^\ominus$ for Br(g) + e^-(g) → Br^- = -331 kJmol^{-1}

$\Delta H_6^\ominus$ for Mg^{2+}(g) + $2Br^-$(g) → $MgBr_2$(s) = ?

$\Delta_f H^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus + \Delta H_5^\ominus + \Delta H_6^\ominus$

Max Born (1882-1970). German physicist, is considered to be one of the founders of modern physics. He was awarded Nobel Prize in physics in 1965 for the interpretation of the wave-function for particles. Fritz Haber (1868-1934), German chemist, developed the process for synthesis of ammonia from atmospheric nitrogen. He received the Nobel Prize in chemistry in 1918.

$\Delta H_6^\ominus = \Delta_f H^\ominus - (\Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus + \Delta H_5^\ominus)$

$= -524 kJ\ mol^{-1} - (+148 + 2187 + 31 + 193 + 2\ (-331))\ kJ\ mol^{-1}$

$= -2421\ KJ\ mol^{-1}$

Hence, Lattice enthalpy $= -\Delta H_6^\ominus = 2421\ kJ\ mol^{-1}$

Some important consequences of lattice enthalpies are:

- The greater the lattice enthalpy, more stable is the ionic compound.
- The lattice enthalpy is greater, for ions of higher charge and smaller radii.
- The lattice enthalpies affect the solubilities of ionic compounds.

6.3 THE COVALENT BOND

The Lewis-Langmuir interpretation of the covalent bond has already been discussed in sections 6.1.1 and 6.1.2. Some of the very important characteristics of chemical bonds are: bond length, bond enthalpy and bond order. We will next discuss briefly these characteristics.

6.3-1 Bond Length

Bond length is defined as the equilibrium internuclear separation distance of the bonded atoms in a molecule. Bond lengths are measured by spectroscopic, x-ray diffraction and electron-diffraction techniques about which you will learn in higher classes. Each atom of the bonded pair contributes to the bond length. In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom.

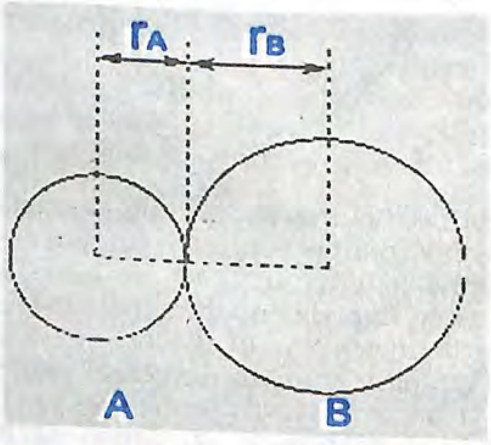


Fig 6.2 The bond length in a covalent molecule AB.

$R = r_A + r_B$

(where R is the bond length and r_A and r_B are the covalent radii of atoms A and B respectively).

In the periodic table the covalent radii increase going down a group and they decrease (for s and p block elements) from left to right across a period. (see Unit 4) **The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom. The van der Waals radius represents the overall size of the atom which includes its valence shell (Fig 6.3).**

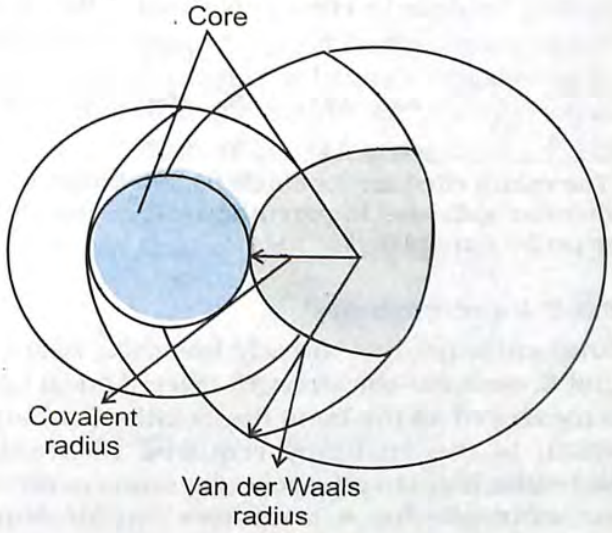


Fig.6.3

Table 6.2 Average bond lengths for some single, double and triple bonds

Bond Type	Bond length (pm)
C-H	107
C-O	143
C=O	121
C-C	154
C=C	133
C≡C	120
C-N	143
C=N	138
C≡N	116
N-O	136
N=O	122
O-H	96

Table 6.3 Bond lengths in some common molecules

Molecule	Bond length (pm)
H_2^+(H- H^+)	106
H_2(H-H)	74
HF(H-F)	92
HCl(H-Cl)	127
HB (H-Br)	141
HI (H-I)	160
N_2 (N≡N)	109
O_2 (O=O)	121
F_2 (F-F)	144
Cl_2 (Cl-Cl)	199
Br_2(Br-Br)	228
I_2 (I-I)	267

Some typical average bond lengths for single,double and triple bonds are shown in **Table 6.2.** Bond lengths for some common molecules are given in **Table 6.3.**

The covalent radii of some common elements are listed in Table 6.4.

Table 6.4 Covalent Radii, * r_{cov}

H	37						
C	77(1)	N	74 (1)	O	66(1)	F	64
	67 (2)		65(2)		57 (2)	Cl	99
	60(3)		55(3)				
		P	110	S	104(1)	Br	114
					95(2)		
		As	121	Se	104	I	133
		Sb	141	Te	137		

* The values cited are for single bonds, except where otherwise indicated in parenthesis. (See also Unit 4 for periodic trends).

6.3-2 Bond Enthalpy

Bond enthalpy has already been discussed in Unit 5, we know the strength of a chemical bond is measured as the bond dissociation enthalpy, which is the enthalpy required to break a particular bond in one mole of gaseous molecule, for example for a homonuclear diatomic molecule like H_2, we have:

$H_2(g) \rightarrow H(g) + H(g)$; $\Delta_a H^\ominus = 435.8$ kJ mol $^{-1}$

Similarly for a heteronuclear diatomic molecule like HCl, we have

$HCl(g) \rightarrow H(g) + Cl(g)$ $\Delta_a H^\ominus = 431.0$ kJ mol^{-1}

For molecules like O_2 and N_2 containing double and triple bonds

$O_2(g)$ (O = O) $\rightarrow O(g) + O(g)$ $\Delta_a H^\ominus = 498.0$ kJ mol^{-1}

N_2(N≡N) (g) $\rightarrow N(g) + N(g)$ $\Delta_a H^\ominus = 946.0$ kJ mol^{-1}

Measurement of strength of bonds in polyatomic molecules is more complicated. In the case of H_2O molecule, for example, the enthalpy needed to break the two O-H bonds is not the same.

$H_2O(g) \rightarrow H(g) + OH(g)$; $\Delta_a H^\ominus_1 = 502$ kJ mol^{-1}

$OH(g) \rightarrow H(g) + O(g)$; $\Delta_a H^\ominus_2 = 427$ kJ mol^{-1}

The difference in the $\Delta_a H^\ominus$ values suggests that the second O-H bond undergoes some change because of a changed chemical environment. This is the reason for some difference in energy of the same O-H bond in different molecules like CH_3OH (methanol) and water. Therefore for polyatomic molecules the term, mean or average bond enthalpy is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken.(See Unit 5).

6.3-3 Bond Order

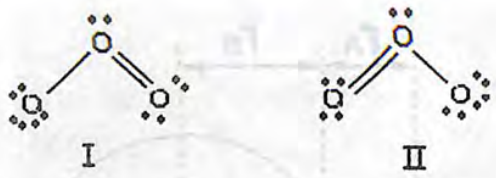
In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in H_2 (with a single shared electron pair), in O_2 (with two shared electron pairs) and in N_2 (with three shared electron pairs) is 1,2,3 respectively. Similarly in CO (three shared electron pairs between C and O) the bond order is 3. For N_2, bond order is 3 and its $\Delta_a H^\ominus$ is 946 kJ mol^{-1} ; being one of the highest for a diatomic molecule.

Isoelectronic molecules and ions have identical bond orders; for example, F_2 and O_2^{2-} have bond order 1. N_2, CO and NO^+ have bond order 3.

A general correlation useful for understanding the stablities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases.

6.3.4 Resonance Structures

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone O_3, molecule can be equally well represented by the structures I and II shown below:



I II

In both structures we have a O-O single bond and an O=O double bond. The normal O-O and O=O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are same (128 pm). Thus the oxygen-oxygen bonds in the O_3 molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

The concept of resonance was introduced to

deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O_3. **According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the resonance hybrid which describes the molecule accurately.** Thus for O_3, the two structures shown above constitute the canonical structures and their hybrid represents the structure of O_3 more accurately. Resonance is represented by a double headed arrow.

Fig.6.4 *Resonance in the O_3 molecule. I and II represent the two canonical forms.*

Some of the other examples of resonance structures are provided by the **carbonate ion and the carbon dioxide molecule.**

Example 6.5
The structure of CO_3^{2-} ion

Solution

The single Lewis structure based on the presence of two single bonds and one double bond between carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds. According to the experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I, II, and III shown below.

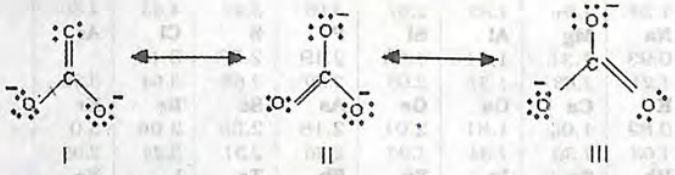


Fig.6.5 *Resonance in CO_3^{2-}, I, II and III represent the three canonical forms.*

Example 6.6
The structure of CO_2 molecule

Solution

The experimentally determined carbon to oxygen bond length in CO_2 is 115 pm. The lengths of a normal carbon to oxygen double bond (C=O) and carbon to oxygen triple bond (C≡ O) are 121 pm and 110 pm respectively. The carbon-oxygen bond lengths in CO_2 (115 pm) lie between the values for C= O and C≡ O. Obviously, a single Lewis structure cannot depict this position and it becomes necessary to write more than one Lewis structures and to consider that the structure of CO_2 is best described as a resonance hybrid of the canonical forms I, II and III.

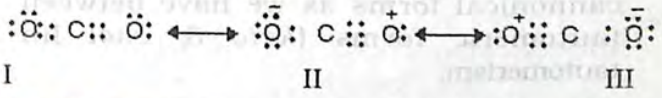


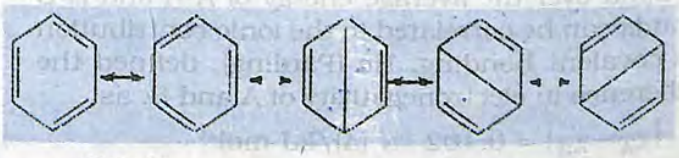
Fig. 6.6 *Resonance in CO_2 molecule, I, II and III represent the three canonical forms.*

In general, it may be said that

- Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single cannonical structure; and,
- Resonance averages the bond characteristics as a whole.

Thus the energy of the O_3 resonance hybrid is lower than either of the two cannonical froms I and II (Fig 6.4).

The individual structures of similar energy contribute equally to the resonance hybrid. Cannonical structures with somewhat higher energies may also contribute to the resultant hybrid, but the higher the energy of a particular structure, the lesser is its contribution. For example in the well known example of benzene molecule (C_6H_6) the cannonical forms are:



Kekule *Dewar*

Fig.6.7 *The two equivalent Kekule forms and three equivalent Dewar forms (The energy of the two Kekule forms is lower than the energy of the three Dewar forms).*

The contribution from the three equivalent Dewar higher energy cannonical forms to the resonance hybrid representing benzene is lesser as compared to the contribution from the two equivalent lower energy Kekule forms.

Many **misconceptions** are associated with resonance and the same need to be dispelled. We have to remember that :

- The cannonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one cannonical form and for other fractions of time in other cannonical forms.
- There is no such equilibrium between the cannonical forms as we have between tautomeric forms (*keto* & *enol*)in tautomerism.
- The molecule as such has a single structure which is the resonance hybrid of the cannonical forms and which cannot as such be depicted by a single Lewis structure.

6.3.5 Electronegativity

The electronegativity, χ is the ability of an atom of an element to attract electrons towards itself in a shared pair of electrons. Thus in a molecule like HF, the highly electronegative fluorine attracts the shared electron pair, between hydrogen and fluorine, towards itself. In other words, the shared electron pair remains more in the vicinity of fluorine than in the vicinity of hydrogen. It may be recalled that in a true covalent bond the electron pair is shared equally between the two atoms, for example in the case of H_2. Thus electronegativity is an important factor which affects the nature of covalent bonds.

Several attempts have been made to formulate a quantitative scale of electronegativity. The **Pauling scale** is based on the energetics of bond formation. According to Pauling, the excess energy, Δ, of a A-B bond over the average energy of A-A and B-B bonds can be correlated to the ionic contribution to covalent bonding. He (Pauling), defined the difference in electronegativity of A and B, as:

$$|\chi_A - \chi_B| = 0.102 \sqrt{(\Delta)/\text{kJ mol}^{-1}}$$

Where $\Delta = E(A\text{-}B) - 1/2 [E(A\text{-}A) + E(B\text{-}B)]$

It follows, that if E(A-B) is markedly different from the average of the covalent (A-A) and (B-B) bonds, then there is a large electronegativity difference between the two atoms A and B.

The **Pauling electronegativities** are directly related to the **oxidation number** (See Unit 9) of the element. Usually the stated values are for the highest oxidation states of elements.

Another useful scale of electronegativity has been proposed by Robert Mulliken. We know that by electron loss or gain an atom becomes a cation or an anion. We also know that electron loss is related to ionization enthalpy, and electron gain to electron gain enthalpy (- time nearly equal to electron affinity). It follows that an atom having a high ionization enthalpy and a low electron gain enthalpy (or high electron affinity) will attract electrons to itself and hence be strongly electronegative. On the other hand an atom with a low ionization enthalpy and a high electron gain enthalpy (low electron affinity) will have a tendency to lose electrons that is it will have little power to attract electrons to itself and therefore will have a small electronegativity. **The Mulliken electronegativity** is given by

$$\chi_M = \tfrac{1}{2} (I + A_e) = \tfrac{1}{2} (\Delta_I H - \Delta_{eg} H)$$

where I = Ionization potential, A_e = Electron affinity

Electronegativity and electron affinity (electron gain enthalpy) though related have different meaning. **Electron affinity refers to an isolated atom's attraction for an additional electron, whereas electronegativity is the attraction of an atom for shared electrons when it is chemically bonded to another atom. The electron affinity is experimentally measurable while electronegativity is a relative number.**

Table 6.5 Pauling and Mulliken* (italics) electronegativities

H 2.20 *3.06*							
Li 0.98 *1.28*	**Be** 1.57 *1.98*	**B** 2.04 *1.83*	**C** 2.55 *2.67*	**N** 3.04 *3.08*	**O** 3.44 *3.22*	**F** 3.92 *4.43*	**Ne** *4.60*
Na 0.93 *1.21*	**Mg** 1.31 *1.63*	**Al** 1.61 *1.37*	**Si** 1.90 *2.03*	**P** 2.19 *2.39*	**S** 2.58 *2.65*	**Cl** 3.16 *3.54*	**Ar** *3.36*
K 0.82 *1.03*	**Ca** 1.00 *1.30*	**Ga** 1.81 *1.34*	**Ge** 2.01 *1.95*	**As** 2.18 *2.26*	**Se** 2.55 *2.51*	**Br** 2.96 *3.24*	**Kr** 3.0 *2.98*
Rb 0.82 *0.99*	**Sr** 0.95 *1.21*	**In** 1.78 *1.30*	**Sn** 1.96 *1.83*	**Sb** 2.05 *2.06*	**Te** 2.10 *2.34*	**I** 2.66 *2.88*	**Xe** 2.6 *2.59*
Cs 0.79	**Ba** 0.89	**Tl** 2.04	**Pb** 2.33	**Bi** 2.02			

* *The Mulliken eletronegativity values are scaled down to match the Pauling values by dividing ½ (I+E) in electron volt by 3.17 .*

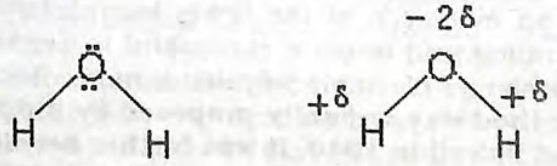
6.3.6 Polarity of Bonds

The existence of a hundred percent ionic or covalent bond represents an ideal situation. In reality no bond (or a compound) is either completely covalent or ionic. Even in the simplest case of the covalent bond between two hydrogen atoms, there is some ionic character (Section 6.5).

In the covalently bonded molecules H_2, Cl_2, F_2, the bond is between atoms of the same element. The bond formed in these molecules by the sharing of an electron pair is infact a classical representation of a covalent bond. However, detailed calculations show that the experimentally determined bond lengths and bond enthalpies can be accounted for only if ionic contributions are also added. In the case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine because the electronegativity of fluorine is far greater than that of hydrogen. This results in the polarization of the bond and of the molecule. We have the formation of a dipolar molecule represented as:

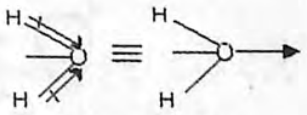
$$\overset{+\delta}{H} - \overset{-\delta}{F}$$

As a result of the polarization, the molecule possesses a dipole moment. A similar situation exists for the triatomic water molecule which has two covalent bonds between the oxygen atom and the two hydrogen atoms. Oxygen with a higher electronegativity attracts the electronic charge to itself and thus oxygen becomes the negative end of the dipole, while the two hydrogens form the positive end. Moreover the lone pairs on oxygen atom also contribute to dipole moment.



H_2O molecule

The bond dipoles and the resultant dipole moment in the water molecule are represented as:

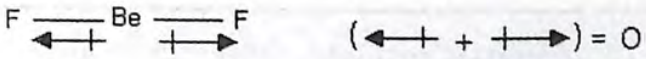


(a) (b)

Net dipole moment $\mu = 1.85D = 6.17 \times 10^{-30}$ C m ($1D = 3.33564 \times 10^{-30}$ C m)

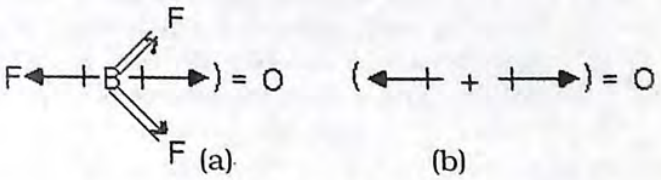
(a) bond dipoles and (b) resultant dipole moment

The dipole moment of a linear molecule like BeF_2 is zero, as the two equal bond dipoles point in opposite directions along a straight line.



Bond dipoles in BeF_2 Total dipole moment in BeF_2

The BF_3 molecule also has a zero dipole moment although the B-F bonds are polar. The three bond moments give a net sum of zero, as the resultant of any two is equal and opposite to the third. In the BF_3 molecule the three F atoms occupy the vertices of an equilateral triangle with the B atom at the centre of the triangle.

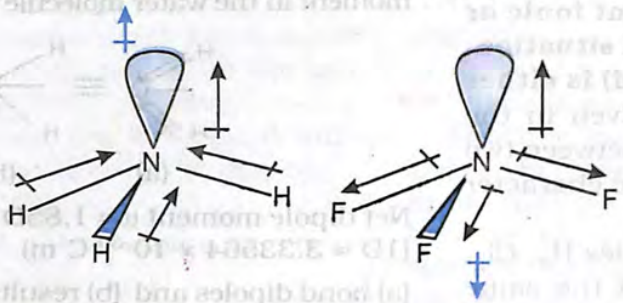


(a) (b)

BF_3 molecule: representation of (a) bond dipoles and (b) total dipole moment

The NH_3 and NF_3 molecules present an interesting case in relation to the resultant dipole moment. Although fluorine is more electronegative than nitrogen the resultant moment of NH_3 (4.90×10^{-30} C m) is greater than that of NF_3 (0.80×10^{-30} C m). In both cases, the central N atom has a lone pair whose bond moment points away from the N atom. As, shown below, it is clear that the dipole moment of NH_3 is larger than that of NF_3.

Resultant dipole moment in $NH_3 = 4.90 \times 10^{-30}$ C m



Resultant dipole moment in $NF_3 = 0.80 \times 10^{-30}$ Cm

Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character.

The partial covalent character of ionic bonds was discussed by Fajans in terms of the following rules:

- The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- The greater the charge on the cation and the anion, the greater the covalent character of the ionic bond.
- For cations of the same size and charge, the one, with an $(n-1)\ d^n\ ns^0$ electronic configuration, typical of transition metals, is more polarising than the one with a noble gas configuration, $ns^2\ np^6$, typical of alkali and alkaline earth metal cations.

The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond, i.e., buildup of electron charge density between the nuclei. The polarising power of the cation, the polarisability of the anion and the extent of distortion (polarisation) of anion are the factors, which determine the percent covalent character of the ionic bond.

6.4 THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY [Shapes (Geometry) of Molecules]

Molecules exist in a variety of shapes. Some of the common geometrical forms are: linear, trigonal planar, tetrahedral, square planar, trigonal-bipyramidal, square pyramidal, octahedral, pentagonal-bipyramidal, and many others.

A number of physical and chemical properties of molecules arise from and are affected by their shapes. For example, the angular shape of the water molecule explains its many characteristic properties which a linear shape does not.

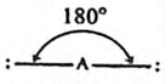
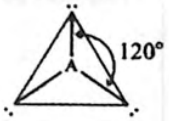
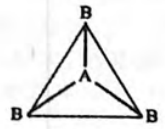
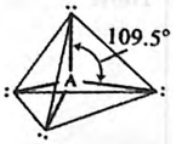
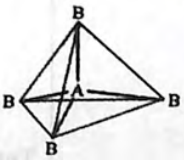
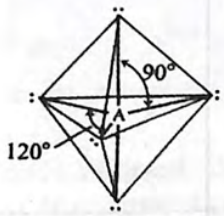
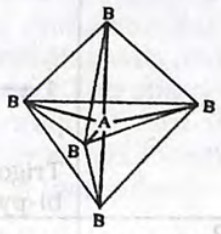
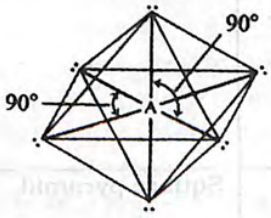
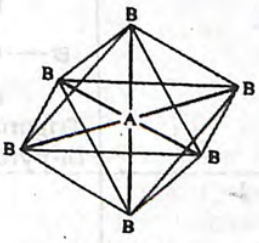
The determination of the molecular geometry and the development of theories for explaining the preferred geometrical shapes of molecules is an integral part of chemical bonding. **The VSEPR theory (model) is a simple treatment for understanding the shapes of molecules.**

Strictly speaking VSEPR theory is not a model of chemical bonding. It provides a simple recipe for predicting the shapes of molecules. It infact is an extension of the Lewis interpretation of bonding and is quite successful in predicting the shapes of simple polyatomic molecules. **The method was orginally proposed by Sidgwick and Powell in 1940. It was further developed and refined by Nyholm and Gillespie (1957).**

The basic assumptions of the VSEPR theory are that:

- Pairs of electrons in the valence shell of a

Table 6.6 Geometry of Molecules in which the central atom has no lone pair of electrons

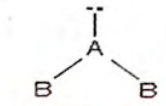
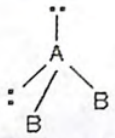
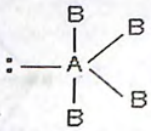
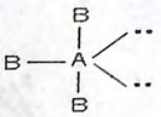
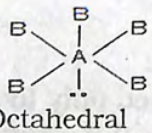
Number of electron pairs	Arrangement of electron pairs	Molecular geometry*	Examples
2	 Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

* The grey lines are used only to show the overall shapes; they do not represent bonds.

central atom repel each other;

- These pairs of electrons tend to occupy positions in space that minimize repulsions and thus maximize distances between them.
- The valence shell is taken as a sphere with the electron pairs localizing on the spherical surface at maximum distances from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can depict a molecule, the VSEPR model is applicable to any such structure.

Table 6.7 Shapes (geometry) of some simple molecules/ions with central ions having one or more lone pairs of electrons.

Molecule Type	No. of Bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape (Geometry)	Examples
AB_2E	2	1	 Trigonal planar	Bent	SO_2, O_3
AB_3E	3	1	Tetrahedral	Trogonal pyramidal	NH_3
AB_2E_2	2	2	 Tetrahedral	Bent	H_2O
AB_4E	4	1	 Trigonal bi-pyramidal	See saw	SF_4
AB_3E_2	3	2	 Trigonal bi-pyramidal	T-shaped	ClF_3
AB_5E	5	1	 Octahedral	Square pyramid	BrF_5
AB_4E_2	4	2	Octahedral	Square planar	XeF_4

For the prediction of geometrical shapes of molecules with the help of VSEPR model, it is convenient to divide molecules into two categories: i) molecules in which the central atom has no lone pairs and ii) molecules in which the central atom has one or more lone pairs. Table 6.6 shows the arrangement of electron pairs about a central atom, A (without any lone pairs) and geometries of some molecules/ions of the type AB_X. Table 6.7 shows geometry of some simple molecules and ions in which the central atom has one on more lone pairs.

Thus as is shown in Table 6.6, in compounds of AB_2, AB_3, AB_4, AB_5 and AB_6, the arrangements of electron pairs and B atoms around the central atom A are: linear, trigonal planar, tetrahedral, trigonal-bipyramidal and octahedral respectively. Such arrangements are present in $BeCl_2$ (AB_2), BF_3 (AB_3), CH_4 (AB_4) and PCl_5 (AB_5) molecules as shown below by their ball-and-stick models.

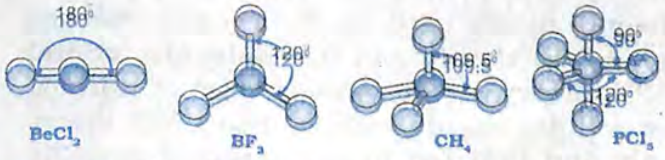
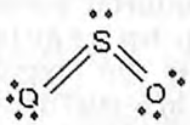


Fig. 6.8 *The shapes of molecules in which central atom has no lone pair*

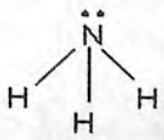
Nyholm and Gillespie (1957) refined the VSEPR model by pointing to the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. Consequently the lone-pair electrons in a molecule occupy more space as compared to the bonding pair electrons. This causes greater repulsion between lone pairs of electrons as compared to the lone pair-bonding pair and bonding pair – bonding pair repulsions. **The descending order of repulsions is:**

(lp-lp)	>	**(lp-bp)**	>	**(bp-bp)**
Lone pair-lone pair	>	**lone pair-bonding pair**	>	**bonding pair-bonding pair**

These repulsion-effects result in deviations from idealized shapes and alterations in bond angles in molecules (Table 6.7). In sulphur dioxide molecule (type AB_2E) there are three electron pairs on the S atom, the overall arrangement is trigonal planar. However because one of the three electron pairs is a lp, the SO_2 molecule has a "bent" shape and because of lp-bp and bp-bp repulsions the angle OSO gets reduced to 119.5° from the value of 120°.

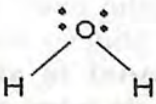


In the ammonia molecule, NH_3, (type AB_3E), there are three bonding pairs and one lone pair. The overall arrangement of four electron pairs is tetrahedral. In NH_3 one of the electron pairs is a lone pair, so the geometry of NH_3 is pyramidal (with the N atom at the apex of the pyramid)

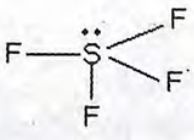


The three NH bonding pairs are pushed closer because of the lp-bp repulsion and the HNH angle gets reduced from 109° 28′ (the tetrahedral angle) to 107°.

The water molecule H_2O, (AB_2E_2 Type) contains two bonding pairs and two lone pairs of electrons. The overall arrangement for four electron pairs is tetrahedral, but the lp-lp, lp-bp and bp-bp repulsions in H_2O reduce the HOH angle to 104.5° and the molecule has a bent shape.

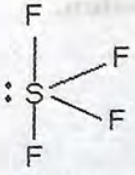


The advantage of Nyholm-Gillespie refinement in predicting the geometry of a molecule accurately is illustrated by the SF_4 molecule. The central sulphur atom has five electron pairs whose arrangement should be trigonal-bipyramidal (Table 6.7). However one of the electron pairs is a lone pair. SF_4 can, therefore, have structure (a) or structure (b) shown below:



(a)

lp in the axial position

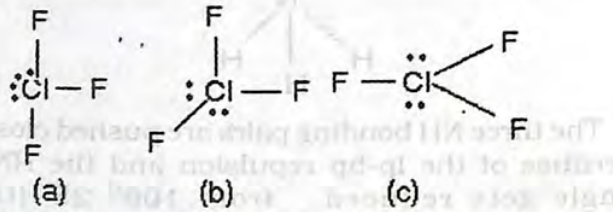


(b)

lp in the equatorial position

In arrangement (a) the lone pair is in an axial position which leads to three lp-bp repulsions at 90°. In structure (b) the lone pair is in an equatorial position and there are only two lp-bp repulsions. Hence arrangement (b) is the favoured structure. The shape shown in structure (b) is variously described as: a distorted tetrahedron, a folded square or a seesaw.

A second example is that of the ClF_3 molecule which is isoelectronic with SF_4. It is also expected to have a basic trigonal bi-pyraimidal (tbp) arrangement of the five electron pairs. However there are two lps and three bps. Three arrangements are possible:



(a) (b) (c)

The two lps in the equatorial plane

One lp in the equatorial and the other in axial position

The two lps in the axial positions

Calculations based on lp-lp, lp-bp and bp-bp repulsions for the three arrangements show that arrangement (a) is the most stable and ClF_3, therefore has a ' T ' shaped structure.

The VSEPR model is able to predict geometries of a large number of molecules, especially of the compounds of *p*-block elements fairly accurately. It is remarkably successful, in predicting geometry quite accurately even where the energy difference between possible structures is very small. The theoretical basis of the VSEPR model regarding the effects of 'electron pair repulsions' on molecular shapes is not clear and continues to be a subject of doubt and discussion.

6.5 VALENCE BOND THEORY

We have already learnt that while the Lewis approach to chemical bonding is useful in writing the structures of molecules, it does not explain why a chemical bond is formed. It gives no reason for the differences in bond dissociation energies and bond lengths in molecules like H_2 (435.8 kJ mol^{-1}; 74 pm) and F_2 (150.6 kJ mol^{-1} ; 142 pm) although in both cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. The Lewis treatment is also silent about the reasons for the different shapes of polyatomic molecules. Similarly the VSEPR model, no doubt a useful method for predicting the geometry of simple molecules, lacks a theoretical basis and has limited applications.

The modern theories of the formation of the covalent bond are essentially based on quantum mechanical principles. The two important theories mostly used are the so called **valence bond** (VB) **theory** and the **molecular orbital** (MO) **theory**. At the present level of learning we will discuss the valence bond (VB) theory only and that too in the simplest possible manner. **The VB theory was introduced by Heitler and London (1927) and developed further by Pauling and others.**

A discussion of the valence bond theory is based on the knowledge of atomic orbitals (Unit 3), electronic configurations of elements (Units 3 and 4), the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. A rigorous treatment of the VB theory in terms of these aspects is beyond the scope of this book. Therefore, for the sake of simplicity, we will restrict the discussion of VB theory to a qualitative, non-mathematical treatment only. To begin with, let us consider the formation of the simplest of all molecules – the hydrogen molecule, H_2.

Linus Carl Pauling (1901-1994). American chemist is regarded as the most influential chemist of the twentieth century. He had a multi-faceted personality. He was awarded the Nobel Prize for Chemistry (1954) and for Peace (1962).

The hydrogen molecule is made up of two hydrogen atoms, that is, a system with two protons (two nuclei) and two electrons each occupying the 1*s* orbital in the respective atoms. According to the VB theory, the H-H, covalent bond is formed by the overlap of the two 1*s* orbitals of the two hydrogen atoms. In very simple terms overlap means that the two orbitals share a common region in space. Further, only two electrons of opposite spins can be present in the overlapping orbitals. In the case of H_2 molecule, the pair of electrons, because of 1s orbital overlap, gets located within a region between the two nuclei. Thus both electrons are attracted by both the nuclei. This along with some other factors results in bond formation between the two H atoms.

A simple interpretation of this process will be that initially when the two H atoms are far apart, there being no interaction between them, the potential energy of the system (the two H atoms) is taken as zero. As the two atoms approach each other, that is, the inter-nuclear separation distance gets reduced, the attraction of the nuclei for the electrons increases and the repulsion between the nuclei as also between the electrons increases. So long as the attraction prevails over repulsion, the potential energy of the system decreases (it becomes negative). (Fig. 6.9). This trend continues till the potential energy of the system reaches a minimum value. This corresponds to the most stable state of the system. It also corresponds to the maximum overlap of the 1s orbitals of the two H atoms, that is to the presence of maximum electron charge density between the two nuclei which leads to the formation of a stable H_2 molecule. Any further decrease in the internuclear distance causes steep increase in the potential energy due to increased internuclear and interelectronic repulsions. Thus, there is an optimum distance, the observed bond distance, at which the total energy of the system is minimum. The decrease in potential energy must be accompanied by a release of energy i.e as the H_2 molecule is formed from two H atoms, heat is given off. It also means that in order to break the H-H bond, energy must be supplied to the molecule.

An important aspect of the VB theory is the criterion of maximum overlap which leads to the formation of the strongest possible bonds. This concept applies equally well to other diatomic molecules also. Thus a stable F_2 molecule forms by the overlap of the 2*p* orbitals of the two F atoms containing unpaired electrons. Similarly the formation of the HF molecule results from the overlap of 1*s* orbital of H and 2*p* orbital of F, both containing unpaired electrons. Since the orbitals involved are not the same in all cases, the bond strengths and bond lengths in H_2, F_2 and HF are different.

The experimentally determined values for the bond enthalpy and bond length for the H-H bond are: 435.8 kJ mol^{-1} and 74 pm respectively. The above mentioned simple theoretical treatment of the formation of the H_2 molecule gives values for bond enthalpy lower than the observed values and bond distance higher than the observed value. In order to match the theoretical and experimental findings, a more rigorous treatment of the formation of the H-H bond is required. Such

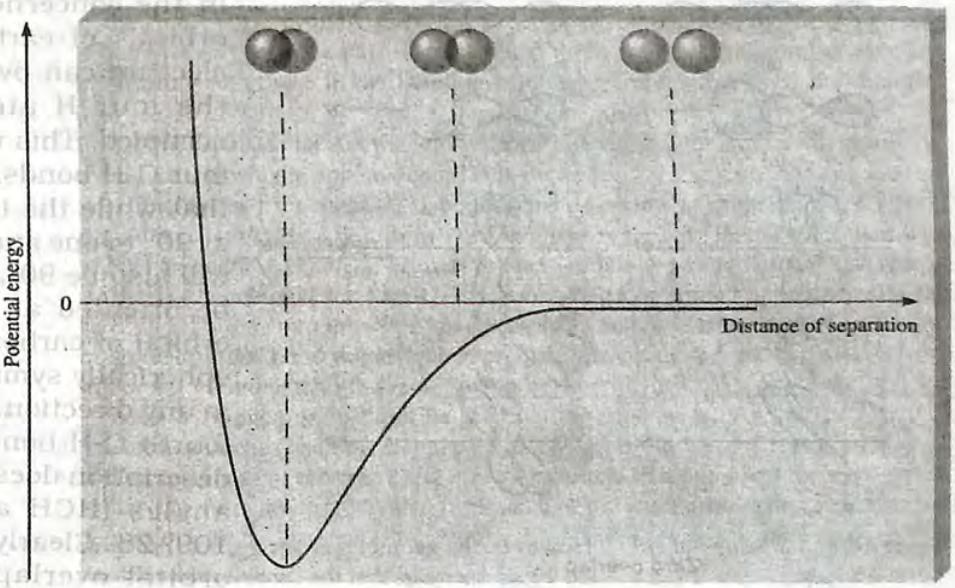


Fig.6.9 *The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.*

a procedure takes into account many other factors besides simple orbital overlap for calculations of bond enthalpy and bond length.

6.5.1 Directional Properties of Bonds

It has been mentioned earlier that covalent bond formation is largely dependent on the overlap of atomic orbitals between atoms. The formation of the H-H covalent bond in H_2 molecule is essentially due to the overlap of the 1s orbitals of the two H atoms when they combine with each other. **In general, the greater the extent of this overlap, the stronger is the bond formed.**

In the case of polyatomic molecules like CH_4, NH_3, and H_2O ; apart from bond formation, the geometry (shape) of the molecules is also to be accounted for. For example, why is it so that CH_4 has a tetrahedral shape and that the HCH angles are $109^0.28'$ in this molecule ?

The valence bond theory explains the formation and the directional properties of bonds in polyatomic molecules like CH_4, NH_3, H_2O, etc; in terms of the important concepts of overlap and hybridization of atomic orbitals. It is, necessary therefore to learn about these two basic concepts.

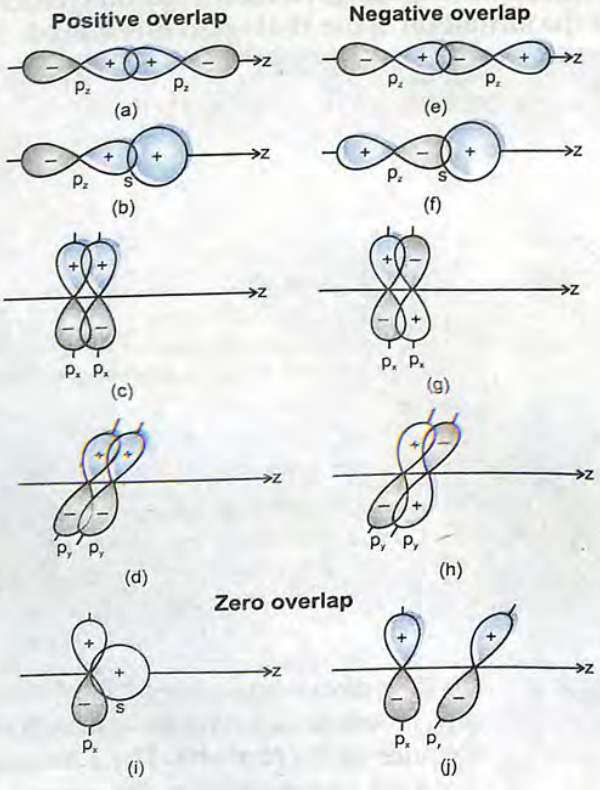


Fig.6.10 *Positive, negative and zero overlaps of s and p atomic orbitals*

6.5.2 Overlap of Atomic Orbitals

Atomic orbital overlaps can be positive, negative or zero depending upon the properties of overlapping atomic orbitals. The various arrangements of *s* and *p*-orbital overlaps resulting in positive, negative and zero overlaps are depicted in Fig.6.10.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. In the case of polyatomic molecules like CH_4, NH_3 and H_2O, the VB theory has to account for their characteristic shapes as well. We know that the shapes of CH_4, NH_3, and H_2O molecules are tetrahedral pyramidal and bent respectively. It would be therefore interesting to find out if these geometrical shapes can be explained in terms of the orbital overlaps.

Let us first consider the CH_4 (methane) molecule. The electronic configuration of carbon in its ground state is $[He]2s^2\ 2p^2$ which in the excited state becomes $[He]\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$. The energy required for this excitation which is later on compensated by the release of energy due to overlap between hybrid orbitals of carbon and the hydrogen is available in the concerned reaction. The four atomic orbitals of carbon, each with an unpaired electron can overlap with the 1s orbitals of the four H atoms which are also singly occupied. This will result in the formation of four C-H bonds. It will, however, be observed that while the three p orbitals of carbon are at 90^0 to one another, the HCH angle for these will also be 90^0. That is three C-H bonds will be oriented at 90^0 to one another. The 2s orbital of carbon and the 1s orbital of H are spherically symmetrical and they can overlap in any direction. Therefore the direction of the fourth C-H bond will be indeterminate. This description does not fit in with the tetrahedral angles (HCH angles) which are equal to $109^0\ 28'$. Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in CH_4. Using similar procedure and arguments, it can be seen that in the case of NH_3 and H_2O molecules, the HNH and HOH angles are 90^0. This is in disagreement with the actual bond angles of 107^0 and 104.5^0 in the NH_3 and H_2O molecules respectively.

6.5.3 Hybridization of Atomic Orbitals

To explain the characteristic geometrical shapes of polyatomic molecules like CH_4, NH_3, H_2O, etc., Pauling introduced the concept of hybridization of atomic orbitals, which constitutes a very important facet of the valence bond theory.

According to Pauling, carbon, nitrogen, oxygen while forming CH_4, NH_3, and H_2O molecules donot use pure atomic orbitals for overlap with the hydrogen 1s orbitals. Instead hybrid orbitals of these atoms are used in bond formation. Combination of the 2s and the three 2p orbitals gives four sp^3 (pronounced as s-p^3) hybrid orbitals mutually oriented at the tetrahedral angle of 109^0 28'. It is these hybrid orbitals which overlap the H 1s orbitals of hydrogen atoms to give the required geometrical shapes of the molecules.

The concept of hybridization is applicable to all types of atomic orbitals. At this level of learning we will focus our attention on the various types of hybridization involving the s and p orbitals only.

The simplest type of *s* and *p* orbital hybridization is the so called *sp* hybridization; also called linear or digonal hybridization. The orbitals suitable for *sp* hybridization are s and p_z orbitals, if the hybrids are to lie along the z-axis. A pictorial representation is given below:

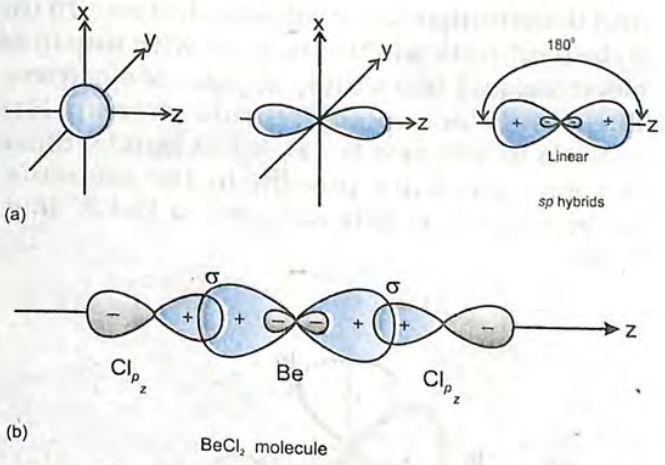


Fig.6.11 *(a) Formation of sp hybrids from s and p orbitals; (b) Formation of the linear $BeCl_2$ molecule*

The two sp hybrids point in opposite directions along the z-axis with protruding positive lobes and very small negative lobes. This provides for more effective overlap resulting in the formation of stronger bonds. The formation of a linear molecule like $BeCl_2$ can easily be explained as shown above.

In the BCl_3 molecule the B-Cl bonds, as shown by experimental data, are coplanar and bond angles are 120^0. On the basis of simple overlap of three atomic orbitals of Be (2s, $2p_x$, $2p_y$) and the three p_x orbitals of chlorine atoms it is not possible to explain the trigonal planar geometry of BCl_3. However if boron were to use sp^2 hybrid orbitals (obtained by mixing of *s*, p_x, p_z orbitals) for bond formation with the three *p* orbitals of chlorine atoms, the geometry of the BCl_3 molecule is easily explained because the sp^2 hybrids are coplanar with angles of 120^0 between them. **sp^2 hybridization; also called trigonal planar hybridization** is shown in Fig.6.12.

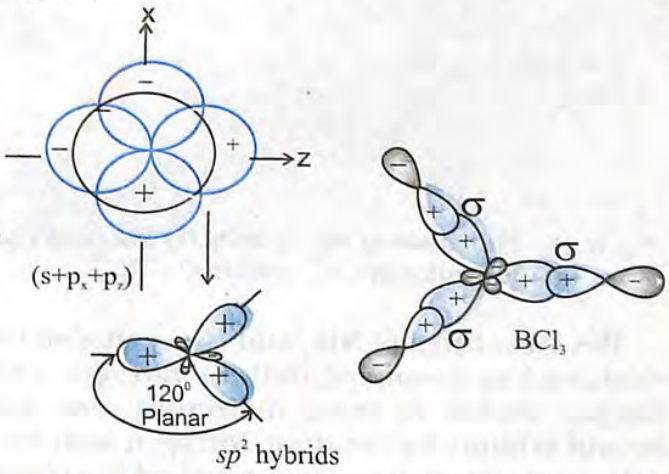


Fig.6.12 *Formation of sp^2 hybrids and the BCl_3 molecule.*

In sp^3 hybridization, also called tetrahedral hybridization, the sp^3 hybrids are obtained by combination of the *s* and three *p* orbitals. The sp^3 hybrid orbitals have a tetrahedral orientation in space, that is, they point towards the four corners of a regular tetrahedron. The tetrahedral angle is 109^0 28'. CH_4 molecule is a convenient example to show the use of sp^3 hybrid orbitals by C atom in forming four C-H two-electron bonds with H atoms. The CH_4 molecule has tetrahedral geometry.

The orbitals suitable for formation of **sp^3 hybrids** are *s*, p_x, p_y, p_z. These four atomic orbitals combine and reform into four sp^3 hybrid orbitals as shown in Fig.6.13.

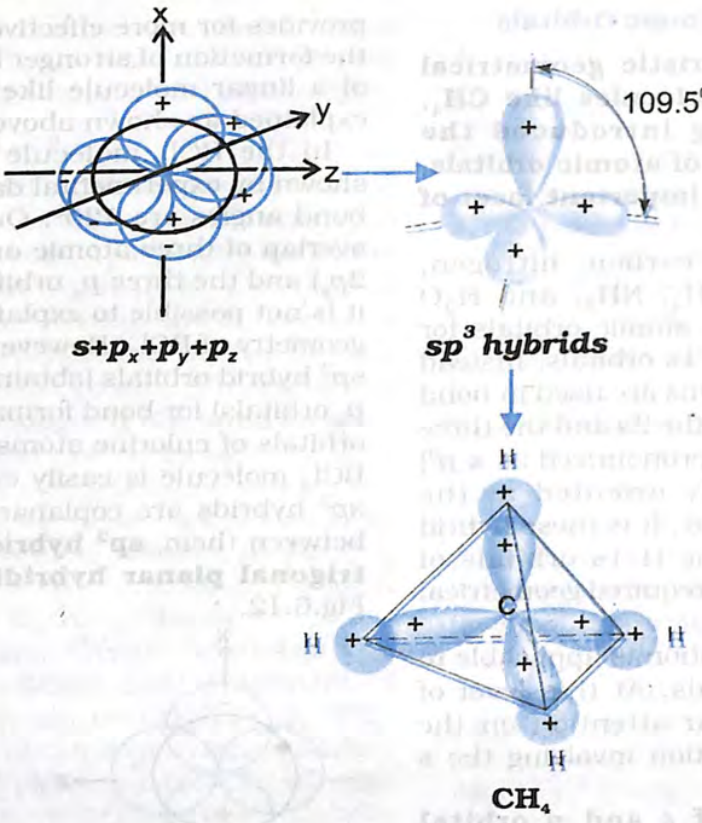


Fig.6.13 *Formation of sp^3 hybrids by the combination of s , p_x , p_y and p_z atomic orbitals of carbon and the formation of CH_4 molecule.*

The structures of NH_3 and H_2O can also be explained by assuming that the nitrogen and oxygen atoms, in these molecules, use sp^3 hybrid orbitals for bonding. Nitrogen with five valence electrons has three unpaired electrons in three sp^3 hybrid orbitals and a lone pair of electrons in the fourth one. The three hydrogen 1*s* orbitals each having an unpaired electron, overlap with the three sp^3 hybrids of N atom thus giving three N-H electron pair bonds. The presence of the lone pair reduces the bond angle to 107^0 due to lp-bp and bp-bp interactions (Fig.6.14). The oxygen in the H_2O molecule is also assumed to be sp^3 hybridized and distribution of six valence electrons in the hybrid orbitals has two hybrids with unpaired electrons and two with lone pairs of electrons. The singly occupied hybrids overlap H1*s* orbitals to give two O – H sigma bonds. Since two lone pairs are present in the molecule, the angle in H_2O gets reduced to 104.5^0 (Fig. 6.15).

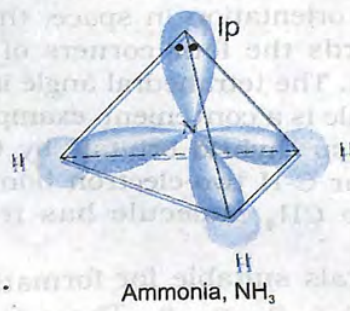


Fig.6.14 *Formation of NH_3 molecule*

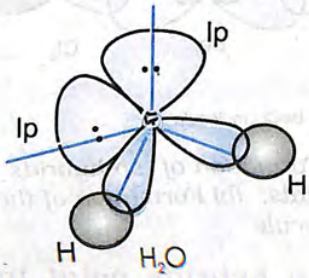


Fig.6.15 *Formation of H_2O molecule*

Carbon has the unique property that it can make use of *sp*, sp^2 or sp^3 hybrid orbitals to form compounds under different conditions. The example of CH_4, wherein carbon uses sp^3 hybrid orbitals has already been discussed above. In **ethene,** C_2H_4, carbon is sp^2 hybridized and one of the *p* orbitals is left as such. The formation of the C_2H_4 molecule (Fig.6.16) can be represented as:

a. Formation of sigma bonds between C and C, and C and H atoms
b. Formation of pi (π) bond between C and C
c. The orbital overlap picture of C_2H_4
d. The orientation of the sigma (σ) bonds and pi bonds
e. The pi electron charge density above and below the C- C sigma (σ) bond.

In the **ethyne,** C_2H_2 , molecule, the carbon atoms use sp hybrids for bonding between carbon and carbon and between C and H atoms. This constitutes the sigma bond frame work of the C_2H_2 molecule. The two unhybridized *p*-orbitals on each carbon atom overlap laterally to give two pi bonds between the carbon atoms. The picture can be represented as in Fig.6.17.

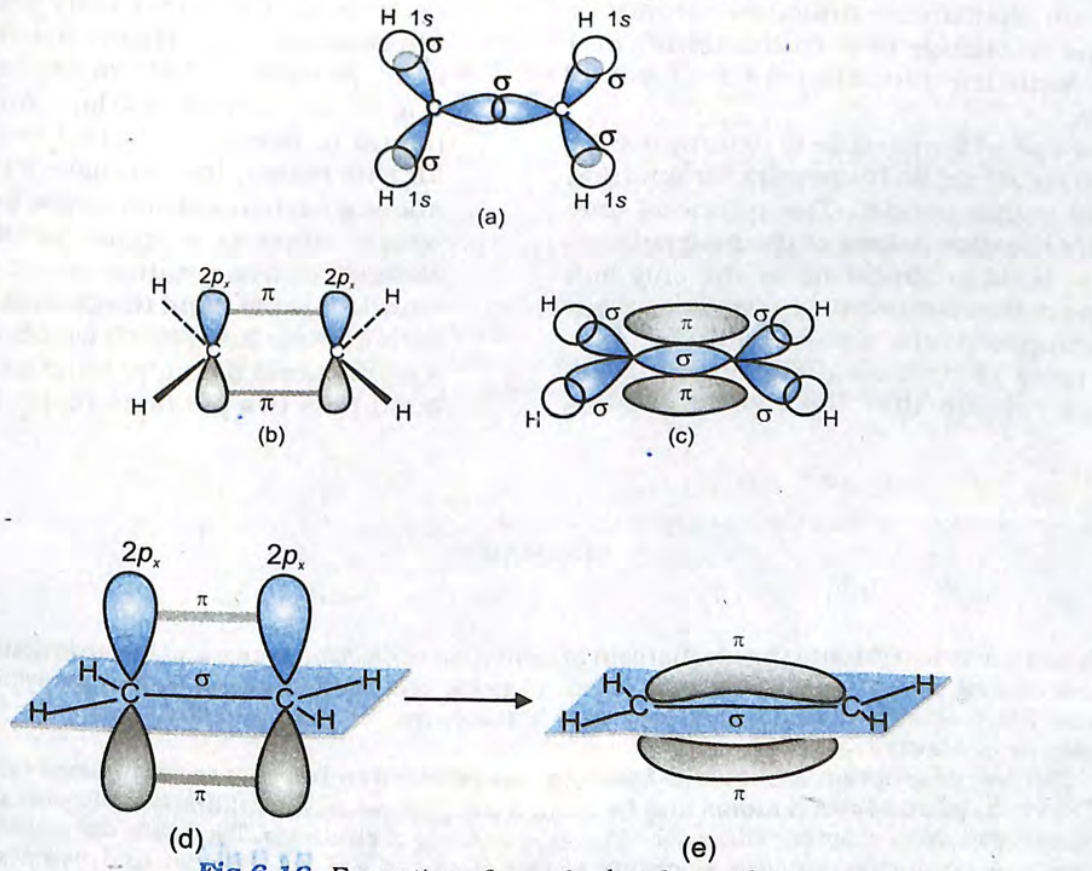


Fig.6.16 *Formation of σ and π bonds in ethene*

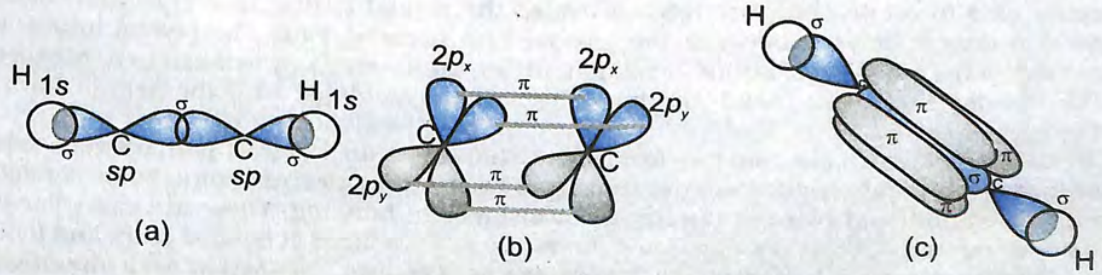


Fig.6.17 *(a) Sigma overlaps (b) Pi overlaps (c) the two pi bonds superimposed on the sigma bond, in ethyne*

The triple bond between the two carbons is made up of one sigma bond and two pi bonds.

From the preceding discussion it follows that :

- It is not necessary that every atomic orbital of carbon occupied by a single electron is used for the formation of hybrid orbitals.
- On account of the lateral overlap of the atomic orbitals and the presence of electronic charge cloud (density) above and below a sigma bond, a pi bond is formed which is weaker than a sigma bond. This is the reason that molecules like C_2H_2 and C_2H_4 readily undergo addition reactions. Each carbon atom here has a tendency to take on additional univalent atoms or groups to change over to the tetrahedral state with the formation of four sigma bonds.
- The shape of a molecule is determined by the so called sigma framework (orientation of the sigma bonds). The pi bonds only modify the dimensions of the molecule.
- The pi bond is almost never the only link between two atoms. It is always present superimposed on a sigma bond.
- The rules of hybridization, among other things require that the hybrid orbitals should be, governed by all the rules applicable to the atomic orbitals. Also the choice of the atomic orbitals for various types of hybridization is essentially determined by their symmetry properties.

The theoretical concept of the sigma and pi bonds is basically linked to the molecular orbital theory. At this stage it may just be noted that a sigma bond results from the end-on overlap of atomic orbitals along the internuclear axis. The pi bonds on the other hand, result from the lateral overlap of atomic orbitals. Free rotation about a sigma bond is possible because the electron density lies along the internuclear axis. This is not true of a pi bond, as there is hindrance to free rotation due to the lateral overlap. Any twist is bound to break the lateral overlap. It is for this reason that we have free rotation about a carbon-carbon single bond (C- C) which infact is a sigma bond and the absence of free rotation about a carbon-carbon double bond (C=C), and a carbon-carbon triple bond (C≡C) which, infact, are a sigma bond plus a pi bond and a sigma bond plus two pi bonds respectively.

SUMMARY

Kossel's first insight into the mechanism of formation of electropositive and electronegative ions related the process to the attainment of noble gas configurations by the respective ions. Electrostatic attraction between ions is the cause for their stability. This gives the concept of **electrovalency**.

The first description of **covalent bonding** was provided by Lewis in terms of the sharing of electron pairs between atoms and he related the process to the attainment of noble gas configurations by reacting atoms as a result of sharing of electrons. The Lewis dot symbols show the number of valence electrons of the atoms of a given element and Lewis dot structures show pictorial representations of bonding in molecules.

An ionic compound is pictured as a three-dimensional aggregation of positive and negative ions in an ordered arrangement called the crystal lattice. In a crystalline solid there is a charge balance between the positive and negative ions. The crystal lattice is stabilized by the enthalpy of lattice formation. Infact, lattice enthalpy is taken as a measure of the stability of an ionic solid and its value can be calculated with the help of Born-Haber cycle.

While a single covalent bond is formed by sharing of an electron pair between two atoms, multiple bonds result from the sharing of two or three electron pairs. Some bonded atoms have additional pairs of electrons not involved in bonding. These are called lone-pairs of electrons. A Lewis dot structure shows the arrangement of bonded pairs and lone pairs around each atom in a molecule. **Important parameters, associated with chemical**

bonds, like: bond enthalpy, bond order, electronegativity and bond polarity have significant effect on the properties of compounds.

A number of molecules and polyatomic ions cannot be described accurately by a single Lewis structure and a number of descriptions (representations) based on the same skeletal structure are written and these taken together represent the molecule or ion. This is a very important and extremely useful concept called **Resonance**. The contributing structures or *canonical forms* taken together constitute the resonance hybrid which represents the molecule or ion.

The ***VSEPR model*** used for predicting the geometrical shapes of molecules is based on the assumption that electron pairs repel each other and, therefore, tend to remain as far apart as possible. According to this model, *molecular geometry is determined by repulsions between lone pairs and lone pairs ; lone pairs and bonding pairs* and *bonding pairs and bonding pairs.* The order of these repulsions being : lp-lp > lp-bp > bp-bp

The **valence bond approach** to covalent bonding is basically concerned with the energetics of covalent bond formation about which the Lewis and VSEPR models are silent. Basically the VB theory discusses bond formation in terms of overlap of orbitals. For example the formation of the H_2 molecule from two hydrogen atoms involves the overlap of the 1s orbitals of the two H atoms which are singly occupied. It is seen that the potential energy of the system gets lowered as the two H atoms come near to each other. At the equilibrium inter-nuclear distance (bond distance) the energy touches a minimum. Any attempt to bring the nuclei still closer results in a sudden increase in energy and consequent destabilization of the molecule. Because of orbital overlap the electron density between the nuclei increases which helps in bringing them closer. It is however seen that the actual bond enthalpy and bond length values are not obtained by overlap alone and other variables have to be taken into account.

For explaining the characteristic shapes of polyatomic molecules Pauling introduced the concept of **hybridization of atomic orbitals**. sp, sp^2, sp^3 hybridizations of atomic orbitals of Be, B,C, N and O are used to explain the formation and geometrical shapes of molecules like $BeCl_2$, BCl_3, CH_4, NH_3 and H_2O. They also explain the formation of multiple bonds in molecules like C_2H_2 and C_2H_4.

EXERCISES

6.1 Write Lewis dot symbols for atoms of the following elements : Be, Na, B. O, N, Br,

6.2 Write Lewis dot symbols for the following ions : Li^+, Cl^-, O^{2-}, Mg^{2+} and N^{3-}

6.3 Write Lewis dot symbols for the following atoms and ions :
S and S^{2-}; P and P^{3-} ; Na and Na^+ ; Al and Al^{3+}; H and H^-

6.4 Draw Lewis structures for the following molecules and ions: PH_3, H_2S, $SiCl_4$, BeF_2, AlI_3, CO_3^{2-}, HCOOH.

6.5 Write the Lewis dot structures of (a) CCl_4, (b) PH_3 and (c) BCl_3. Is the octet rule obeyed in these structures ?

6.6 Predict the shapes of the following molecules using the VSEPR model : $BeCl_2$, $SiCl_4$, AsF_5, H_2S, PH_3.

6.7 Discuss the shapes of the following molecules on the basis of valence bond theory : BeF_2, H_2O, NH_3, CH_4.

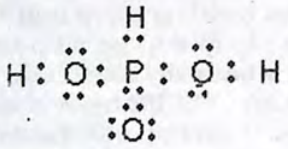
6.8 Draw the shapes of the following hybrid orbitals: sp, sp^2, sp^3.

6.9 Explain the formation and difference between a sigma bond and a pi bond.

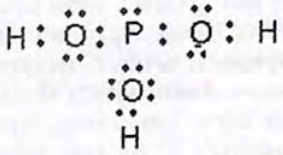
6.10 Explain how the valence bond theory accounts for
(i) a carbon – carbon double bond (C = C)
(ii) a carbon – carbon triple bond (C ≡ C)

6.11 Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

6.12 H_3PO_3 can be represented by the structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3 ? If not, cite reasons for the same.



(1)



(2)

6.13 Draw Lewis structures for H_2CO_3, SF_6, PF_5, IF_7 and CS_2. Is the octet rule obeyed in these cases ?

6.14 Write resonance structures for SO_3, NO_2, and NO_3^-.

6.15 Use Lewis dot symbols to show electron transfer between the following atoms to form cations and anions: (a) Na and Cl, (b) K and S, (c) Ca and O, (d) Al and N, (e) Li and H.

6.16 Define lattice enthalpy. How is it related to the stability of an ionic compound ?

6.17 How can the lattice enthalpy of an ionic compound like NaCl be determined by using the Born-Haber cycle ?

6.18 Calculate the lattice enthalpy of LiF given that the enthalpy of: (i) sublimation of Lithium is 155.2 kJ mol^{-1}; (ii) dissociation of ½ mole of F_2 is 75.3 kJ; (iii) Ionization of lithium is 520 kJ mol^{-1}; (iv) Electron gain of 1 mol of F(g) is -333 kJ; (v) $\Delta_f H^\ominus$ overall is –594.1 kJ mol^{-1}.

6.19 Calculate the lattice enthalpy of $CaCl_2$, given that the enthalpy of: (i) sublimation of Ca is 121 kJ mol^{-1}; (ii) dissociation of Cl_2 to Cl is 242.8 kJ mol^{-1} (iii) ionization of Ca to Ca^{2+} is 2422 kJ mol^{-1} ; (iv) electron gain for Cl to Cl^- is –355 kJ mol^{-1} and (v) $\Delta_f H^\ominus$ overall is –795 kJ mol^{-1}.

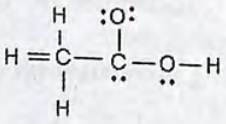
6.20 Define electronegativity, How does it differ from electron affinity ?

6.21 What is a polar covalent bond? Give two examples of compounds containing polar covalent bonds.

6.22 Arrange the bonds in order of increasing ionic character in the molecules: LiF; K_2O; N_2, SO_2 and ClF_3.

6.23 Arrange the following bonds in the order of increasing ionic character: C—H , F—H, Br—H, Na—I, K—F and Li—Cl

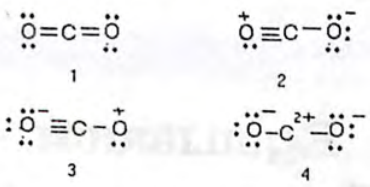
6.24 The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are wrongly shown. Write the correct Lewis structure for acetic acid.



6.25 Define bond length, resonance and resonance structure.

6.26 What are the guidelines for writing resonance structures ?

6.27 Out of the following four resonance structures for the CO_2 molecule, which are important for describing the bonding in the molecule and why ?



1 2 3 4

6.28 Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why CH_4 is not square-planar?

6.29 Why is it that in the SF_4 molecule, the lone pair of electrons occupies an equatorial position in the overall trigonal bi-pyramidal arrangement in preference to an axial position.

6.30 Explain why BeH_2 molecule has a zero dipole moment although the Be-H bonds are polar.

6.31 Sketch the bond moments and resultant dipole moments in the following molecules: H_2O, PCl_3, NH_3, NF_3.

6.32 Explain how VB theory differs from the Lewis concepts.

6.33 What is meant by hybridization of atomic orbitals? Describe the change in hybridization (if any) of the Al atom in the following reaction $AlCl_3 + Cl^- \rightarrow AlCl_4^-$.

6.34 Is there any change in the hybridization of the B and N atoms as a result of the following reaction: $BF_3 + NH_3 \rightarrow F_3B - NH_3$?

6.35 Draw diagrams showing the formation of a double and a triple bond between carbon atoms in the C_2H_4 and C_2H_2 molecules.

6.36 What is the total number of sigma bonds and pi bonds in the following molecules:

C_2H_3Cl, CH_2Cl_2, $H_3C-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-C\equiv C-H$

6.37 Considering x- axis as the internuclear axis which out of the following will form a sigma bond: (a) 1*s* and 1*s*; (b) 1*s* and $2p_x$; (c) $2p_y$ and $2p_y$, (c) $2p_x$ and $2p_y$; (d) 1*s* and 2*s*.

6.38 Which hybrid orbitals are used by carbon atoms in the following molecules:

(a) H_3C-CH_3; (b) $H_3C-CH=CH_2$; (c) CH_3-CH_2-H ; (c) CH_3-CHO; (d) CH_3COOH

6.39 What is meant by the term bond order in Lewis concept? Calculate the bond order of: N_2, O_2 and CO.

6.40 Write formal charges of the atoms in the carbonate ion.

6.41 Write formal charges of the atoms in the nitrite ion.

6.42 The dipole moment of hydrogen halides decreases from HF to HI. Explain this trend.

6.43 Sketch the bond moments and resultant dipole moments in SO_2, *cis*- and *trans* forms of $C_2H_2Cl_2$.

6.44 Which out of the two molecules OCS and CS_2 has a higher dipole moment and why?

UNIT 7

EQUILIBRIUM - I

EQUILIBRIUM IN PHYSICAL AND CHEMICAL PROCESSES

Objectives

After studying this Unit, you will be able to

- explain the dynamic nature of equilibrium in physical and chemical processes.
- state and explain the law of chemical equilibrium.
- write the expression for equilibrium constant for a given reaction.
- use equilibrium constant for predicting the extent of a chemical change.
- explain the terms pure solid and pure liquid in a chemical reaction and apply the same in equilibrium constant expressions.
- establish a relationship between K_p and K_c.
- explain the effect of concentration, pressure and temperature on the equilibrium state.
- explain the role of catalyst on establishing the equilibrium state.

"What can we do when we cannot g backward or forward ?

We have noted in Unit-2 that when liquid water is introduced into an evacuated closed vessel at a particula temperature, it starts evaporating and vapour pressur of water increases till it becomes constant. We say tha the system has reached equilibrium state at this stag However, as we have mentioned in Unit-2, this is not stati equilibrium and there is lot of activity at the boundar between the liquid and the vapours. Water molecules wit relatively higher kinetic energy, escape the liquid surfac into the vapour phase and an equal number of wate molecules from the vapour phase strike the liquid surfac and are retained in the liquid phase. Thus, there is *dynamic equilibrium*, and at this stage, the rate evaporation is equal to the rate of condensation. It ma be represented by

$$H_2O(l) \rightleftharpoons H_2O(vap)$$

The double arrows indicate that the processes in bot the direction are going on simultaneously.

It is not only for a physical process that equilibrium established but the same is true for a chemical reactio If we take pure reactants in a closed vessel at a particula temperature, they start reacting to give products. Th reaction may be fast or slow depending on the experimenta conditions and the nature of the reactants. However, on thing is sure that the concentration of the reactants keep on decreasing, while that of the products keeps o increasing for some time after which there is no chang in the concentration of either of the reactants or products At this stage the system attains dynamic equilibrium an the rates of the forward and reverse reactions becom equal. This explains, why there is no change in th concentration of various species in the reaction mixture In spite of a large number and variety of chemical

reactions, their state of chemical equilibrium may be classified in three groups characterized by the extent to which the reactions proceed.

(i) In the first group we have reactions that proceed nearly to completion and only negligible concentration of the reactants is left. In some cases the concentration of the reactants may be so small that it may not be even possible to detect these experimentally.

(ii) In the second group, we have reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.

(iii) In the third group we have reactions in which the concentrations of the reactants and products are comparable when the system is in equilibrium.

The extent of a reaction in equilibrium depends on the experimental conditions. It is very important in industry and laboratory to optimize operational conditions so that equilibrium is favourable in the direction of the desired product. In the isolation of the pure product from the reaction mixture, we have to rely on different physical processes like evaporation, crystallization etc.

We shall consider in this Unit some important aspects of equilibrium involving physical and chemical processes.

7.1 EQUILIBRIUM IN PHYSICAL PROCESSES

The characteristics of system at equilibrium are better understood if we examine some physical processes. The most familiar examples are phase transformation processes, e.g.

solid $\rightleftharpoons$ liquid

liquid $\rightleftharpoons$ gas

solid $\rightleftharpoons$ gas

7.1.1 Solid-Liquid Equilibrium

Ice and water placed in a perfectly insulated thermos flask (assuming there is no exchange of heat between its contents and the surroundings) at 273 K and at normal atmospheric pressure are in equilibrium state and the system shows interesting characteristics features. First, we notice that the mass of ice and water do not change and the temperature remains constant. However, the equilibrium is not static and if we could observe the individual molecules of ice and water then intense activity can be noticed at the boundary between ice and water. Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at 273 K and 1 atm.

It is obvious that ice and water are in equilibrium only at a particular temperature and pressure. *For any pure substance at atmospheric pressure the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance.* Freezing point of a substance changes only slightly with pressure. The system here is in dynamic equilibrium and we can infer the following:

(i) Both the opposing processes occur simultaneously.

(ii) Both the processes occur at the same rate so that the amount of the substance on both sides remains constant.

7.1.2 Liquid-Vapour Equilibrium

It is common experience that even though the temperature of Delhi (or Jaipur or Hyderabad) and the temperature of Mumbai (or Chennai or Kolkata) be the same on a particular day, one sweats more at Mumbai (or Chennai or Kolkata), especially during the summer months. We usually say that the humidity is high in cities close to sea or any large body of water. The following simple experiment can help us in understanding this phenomenon.

A transparent box carrying a U-tube with mercury (manometer), is made dry by placing some drying agent like anhydrous calcium chloride (or phosphorus penta-oxide) for a few hours and then removing the drying agent (Fig. 7.1). By tilting the box on one side, a watch glass (or petri dish) containing water is quickly pushed inside the box. We then watch the manometer. It will be observed that the fluid level in the right limb of the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. You may also notice, that the volume of water in the watch glass decreases.

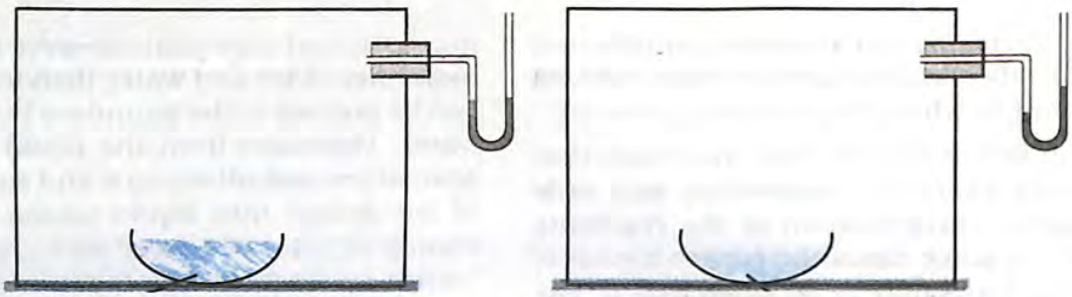


Fig.7.1 Measuring equilibrium vapour pressure of water at a constant temperature.

Initially, there is no water vapours (or very little) inside the box and as water evaporates the pressure in the box increases due to the addition of water molecules into the gaseous phase inside the box. The rate of evaporation is constant. However, the rate of increase in pressure decreases with time leading to equilibrium condition when there is no net evaporation. This implies that as the number of water molecules in the gaseous state increases, the rate of condensation of water molecules from the gaseous state into the liquid state also increases till equilibrium is attained, i.e.

rate of evaporation = rate of condensation

or $H_2O(l) \rightleftharpoons H_2O(vap)$

At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the **equilibrium vapour pressure** of water (or just vapour pressure of water). vapour pressure of liquid increases with temperature. If the above experiment is repeated with different amounts of water in watch glass, the final equilibrium vapour pressure at a given temperature is independent of the amount of water in the watch glass as long as even a small amount of liquid water is present in it at equilibrium.

If the experiment is repeated with methyl alcohol and acetone, it would be noticed that different liquids have different *equilibrium vapour pressure* at the same temperature, and the liquid which has a higher vapour pressure is more volatile. If we expose three watch glasses containing separately 1 mL each of acetone, ethyl alcohol and water to atmosphere and repeat the experiment with different volumes of the liquids in a warmer room. It is observed that in all such cases the liquid eventually disappears and the time taken for complete evaporation depends on the *nature of the liquid, the amount of the liquid* and *the temperature.* When the watch glass is open to the atmosphere, the rate of evaporation remains constant but the molecules are dispersed into large volume of the room, the rate of condensation from vapour to liquid state is less than the rate of evaporation. These are open systems (Unit-5) and it is not possible to reach equilibrium in an open system.

Our atmosphere is an open system and the water vapour in the air would depend on the amount of water in the area, the wind velocity, temperature, etc. Near a sea or a lake, especially when the wind is not high, the amount of water vapour in the air at a given temperature is high (as in Kolkata, Mumbai or Chennai) compared to a city in Rajasthan (almost a desert), Delhi or Hyderabad.

Example 7.1

Vapour pressure of water, acetone and ethanol at 293 K are 2.34, 12.36 and 5.85 kPa respectively. Which of these has the lowest and the highest boiling point ? At 293 K which of these evaporates least in a sealed container before equilibrium is established?

Solution

We know that when temperature rises, vapour pressure of a liquid also rises and at boiling point, vapour pressure becomes equal to atmospheric pressure. A liquid with lower vapour pressure will require higher temperature for it to attain its vapour pressure equal to atmospheric pressure. Therefore, the liquid with the highest vapour pressure will have the lowest boiling point. Acetone has the lowest boiling point and water has the highest boiling point.

At 293 K, water evaporates least in the sealed container before equilibrium is established.

7.1.3 Equilibrium Involving Dissolution of Solids or Gases in Liquids

Solids in Liquids: It is common knowledge that we can dissolve only a limited amount of salt or sugar in a given amount of water. If we make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals separate out if we cool the syrup. We call it a *saturated solution* when no more of solute can dissolve in it at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature. In a saturated solution, a dynamic equilibrium exists between the solute molecules in the solid state and in the solution.

Sugar (solution) ⇌ Sugar (solid)

And at equilibrium,

Rate of dissolution of sugar = Rate of crystallization of sugar

Equality of the two rates and dynamic nature of equilibrium has been confirmed with the help of *radioactive sugar* (Fig.7.2). If we drop some radioactive sugar into saturated solution of non-radioactive sugar, then after some time radioactivity is observed both in the solution and solid sugar. Initially there were no radioactive sugar molecules in the solution but due to dynamic nature of equilibrium, there is exchange between the radioactive and non-radioactive sugar molecules between the two phases. Therefore the ratio of the radioactive to non-radioactive molecules in the solution increases till it attains a constant value.

Gases in Liquids: We are aware that when a soda water bottle is opened, some of the carbon dioxide gas dissolved in it fizzes out rapidly. The phenomenon arises due to difference in solubility of carbon dioxide at different pressures. There is equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid. For example,

CO_2 (gas) ⇌ CO_2 (in solution)

This kind of equilibrium is governed by **Henry's law**. It states that ***the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent***. This amount decreases with increase of temperature. The soda bottle is sealed under pressure of gas when its solubility in water is high. As soon as the bottle is opened, some of the dissolved carbon dioxide gas escapes to reach a new equilibrium condition required for the lower pressure, namely its partial pressure in the atmosphere. If you leave the soda water bottle open to the air for some time, the gas escape and it turns 'flat'.

Example 7.2

0.200 g of iodine is stirred in 100mL of water at 288 K till equilibrium is reached. What will be the mass of iodine found in solution and the mass that is left undissolved ? After equilibrium is reached with 0.200g of iodine in 100 mL of water, we add 150 mL of water to the system. How much iodine will be dissolved and how much will be left undissolved and what will be the concentration of iodine in solution?

$[I_2(aq)]_{\text{at equilibrium}} = 0.0011 \text{ mol L}^{-1}$ at 288 K

Solution

Molar mass of iodine, I_2 = 254 g mol^{-1}

At equilibrium the amount of iodine dissolved in 1 litre of water

= 0.0011 mol L^{-1} × 254 g mol^{-1}

= 0.2794 g L^{-1}

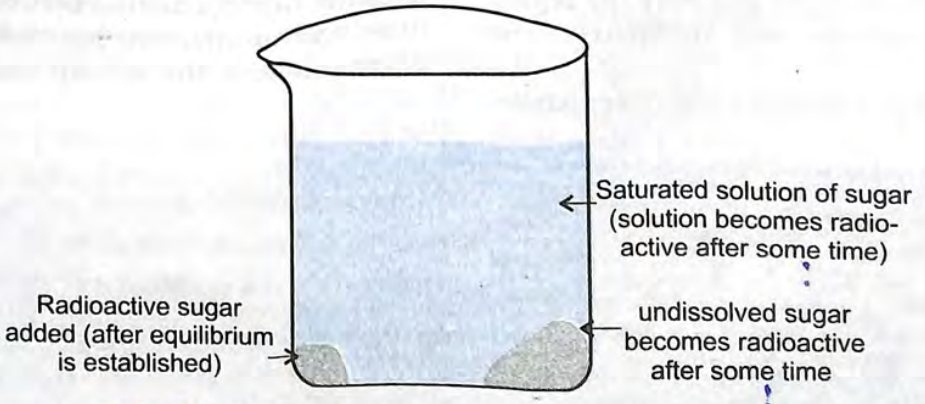

Saturated solution of sugar (solution becomes radio-active after some time)
Radioactive sugar added (after equilibrium is established)
undissolved sugar becomes radioactive after some time

Fig.7.2 Demonstration for dynamic nature of equilibrium.

$\cong 0.28\ g\ L^{-1}$

Therefore, mass of dissolved iodine in 100 mL
= 0.028 g

Mass of undissolved iodine in 100 mL
= (0.200 – 0.028)g = 0.172 g

After equilibrium between 0.200 g of I_2 and 100 mL of water is reached, addition of 150mL of water will result in further dissolution of I_2.

Volume of solution after addition of 150 mL of water = 100mL + 150 mL = 250mL

Now dissolved iodine in 250 mL of water

$$= \frac{0.28g \times 250mL}{1000mL} = 0.070g \text{ of iodine}$$

Undissolved iodine =0.200g –0.070 g =0.130 g.

Molar Concentration

$$= \frac{0.070g}{254\ g\ mol^{-1} \times 250mL} \times \left(\frac{1000mL}{1L}\right)$$

$$= 0.0011\ mol\ L^{-1}$$

7.1.4 General Characteristics of Equilibria Involving Physical Processes

It has been noted that

(i) for liquid ⇌ vapour equilibrium, the vapour pressure is constant at a given temperature.

(ii) for solid ⇌ liquid equilibrium, there is only one temperature (melting point) at 1 atm at which the two phases can coexist. If there is no exchange of heat with the surroundings, the mass of the two phases remain constant.

(iii) for dissolution of solids in liquids the solubility is constant at a given temperature.

(iv) for dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid.

These observations are summarized in Table 7.1.

For the physical processes discussed above, following characteristics are common to the **System at equilibrium**:

(i) Equilibrium is possible only in a closed system at a given temperature.

(ii) Both the opposing processes occur at the same rate and there is a dynamic but stable condition.

(iii) All measurable properties of the system remain constant.

(iv) When equilibrium is attained for a physical process, it is characterized by constant value of one of its parameters at a given temperature. Table 7.1 lists such quantities.

(v) The magnitude of such quantities at any stage indicates the extent to which the reaction has proceeded before reaching equilibrium.

7.2 EQUILIBRIUM IN CHEMICAL PROCESSES — DYNAMIC EQUILIBRIUM

As mentioned earlier, chemical reactions carried out in a closed system eventually reach a state of equilibrium. This equilibrium, as in physical systems, is dynamic in nature. The dynamic equilibrium consists of a *forward reaction* in which reactants give product(s) and *reverse reaction* in which products give the original reactant(s).

Let us consider a general case of a reversible reaction

$$A + B \rightleftharpoons C + D \qquad (7.1)$$

Where A and B react, their concentration as well as the rate of forward reaction decreases as the time passes.

As the concentrations of C and D build up, they start reacting to form A and B

$$C + D \rightarrow A + B \qquad (7.2)$$

As the concentration of C and D increases so does the rate of reaction between C and D with time. Eventually, two reactions occur at the same rate and the system reaches a state of

Table 7.1 Some Features of Physical Equilibria

Process	Conclusion
H_2O (l) ⇌ H_2O (g)	PH_2O Constant at given temperature
H_2O (s) ⇌ H_2O (l)	Melting point is fixed at constant pressure
Solute (s) ⇌ Solute (solution)	Concentration of solute in solution is constant at a given temperature
Gas (g) ⇌ gas (aq)	[gas (aq)]/[gas (g)] is constant at a given temperature
(For example, CO_2(g) ⇌ CO_2(aq)	[CO_2 (aq)]/[CO_2(g)] is constant at a given temperature

equilibrium (Fig.7.3).

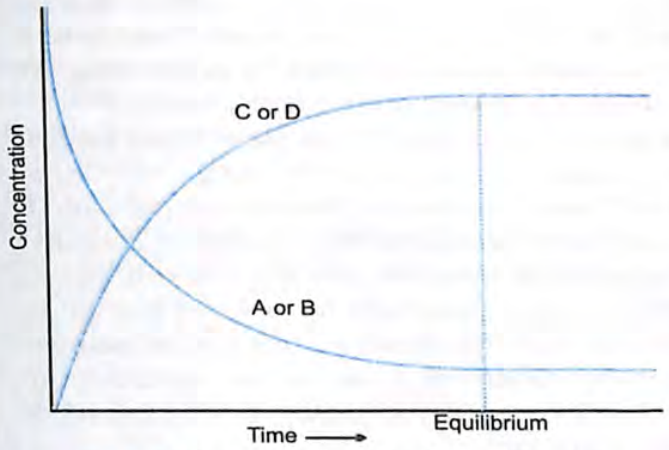


Fig.7.3 *Attainment of chemical equilibrium*

$A + B \rightleftharpoons C + D$

The same state of equilibrium is reached if we start with C and D when no A and B are present initially. Even after the equilibrium is attained, forward and reverse reactions continue to take place at equal rates and do not stop and the equilibrium can be attained from either direction.

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. In a series of experiments, Haber started with known amounts of nitrogen and hydrogen maintained at high temperature and pressure and at regular intervals determined the amount of ammonia present. He was successful in determining also the concentration of unreacted hydrogen and nitrogen. Fig.7.4 shows that after a certain time the composition of the mixture remains the same even though some of the reactants are still present. This constancy in composition indicates that the reaction has reached equilibrium. In order to understand the dynamic nature of the reaction, synthesis of ammonia was carried out with exactly the same starting conditions (of partial pressure and temperature but using D_2 (deuterium) in place of H_2). The reaction mixtures starting either with H_2 or D_2 reach equilibrium with the same composition, except that D_2 and ND_3 are present instead of H_2 and NH_3. After equilibrium is attained, these two mixtures (H_2, N_2, NH_3 and D_2, N_2, ND_3) are mixed together and left for a while. When later this mixture is analyzed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analyzed by a mass spectrometer, it is found that all duterium containing forms of ammonia (NH_3, NH_2D, NHD_2 and ND_3) and hydrogen (H_2, HD and D_2) are present. Thus one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way.

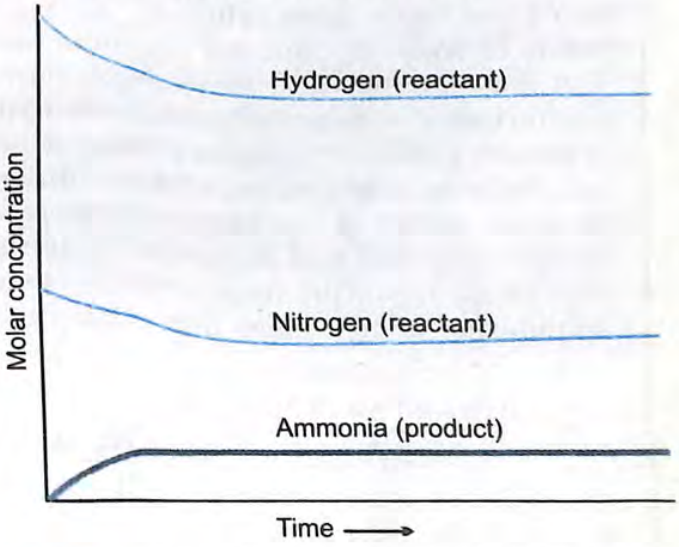


Fig.7.4 *Depiction of equilibrium for the reaction* $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Use of isotope (deuterium) in the formation of ammonia clearly indicates that **chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.**

Equilibrium can be attained from both sides, whether we start reaction by taking, $H_2(g)$ and $N_2(g)$ and get $NH_3(g)$ or by taking $NH_3(g)$ which will decompose into $N_2(g)$ and $H_2(g)$.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

Similarly let us consider the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. If we start with equal initial concentration of H_2 and I_2, the reaction proceeds in the forward direction and the concentration

Dynamic Equilibrium – A Student's Activity

Equilibrium whether in a physical or in a chemical system, is always of dynamic nature. This can be demonstrated by the use of radioactive isotopes. This is not feasible in a school laboratory. However this concept can be easily comprehended by performing the following activity. The activity can be performed in a group of 5 or 6 students.

Take two 100mL measuring cylinders (marked as 1 and 2) and two glass tubes each of 30 cm length. Diameter of the tubes may be same or different in the range of 3-5mm. Fill nearly half of the measuring cylinder-1 with coloured water (for this purpose add a crystal of potassium permanganate to water) and keep second cylinder (number 2) empty. Put one tube in cylinder 1 and second in cylinder 2. Immerse one tube in cylinder 1, close its upper tip with a finger and transfer the water contained in its lower portion to cylinder 2. Using second tube, kept in 2nd cylinder, transfer the water in a similar manner from cylinder 2 to cylinder 1. In this way keep on transferring coloured water using the two glass tubes from cylinder 1 to 2 and from 2 to 1 till you notice that the level of coloured water in both the cylinders becomes constant.

If you continue intertransferring coloured solution between the cylinders, there will not be any further change in the levels of coloured water in two cylinders. If we take analogy of 'level' of coloured water with 'concentration' of reactants and products in the two cylinders, we can say the process of transfer, which continues even after the constancy of level, is indicative of dynamic nature of the process. If we repeat the experiment taking two tubes of different diameters we find that at equilibrium the level of coloured water in two cylinders is different. How far diameters are responsible for change in levels in two cylinders? Empty cylinder (2) is an indicator of no product in it at the beginning.

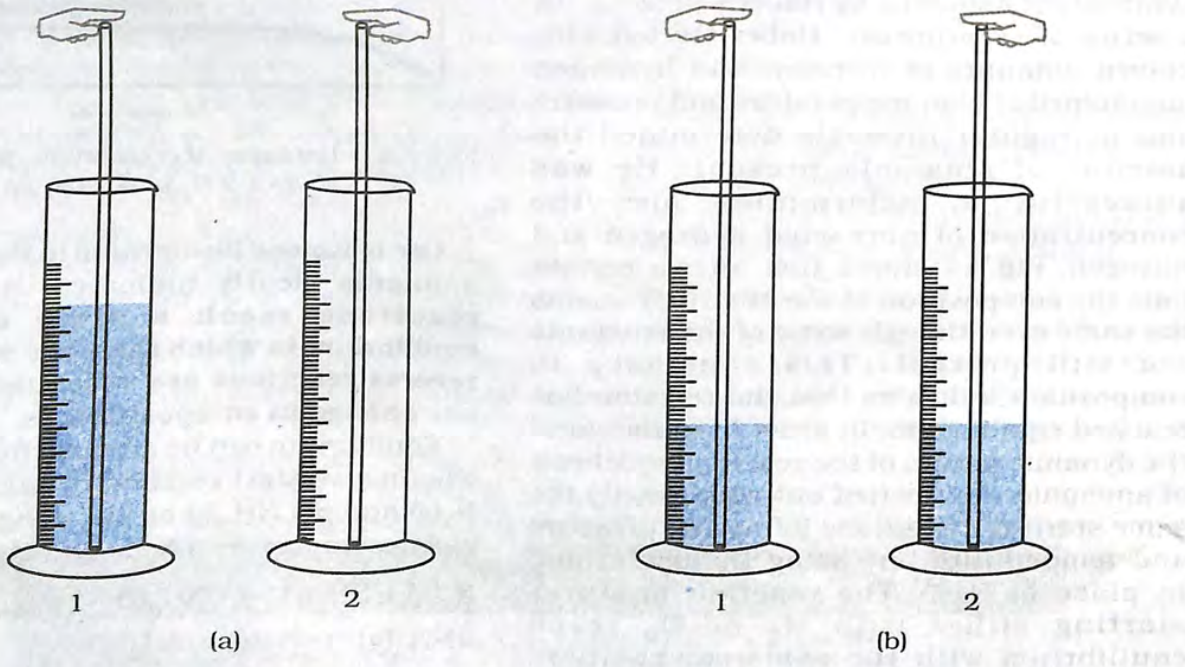


Fig.7.5 *Demonstrating dynamic nature of equilibrium. (a) initial stage (b) final stage after the equilibrium is attained.*

of H_2 and I_2 decreases while that of HI increases, until all of these become constant at equilibrium. We can also start with HI alone and the reaction proceeds in the reverse direction, concentration of HI decreases and concentration of H_2 and I_2 increases until they all become constant when equilibrium is reached (Fig.7.6). If total number of H and I atoms are same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants or pure product.

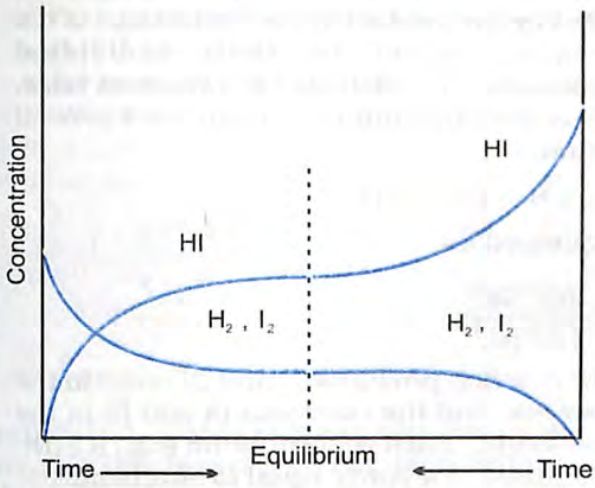


Fig.7.6 *Chemical equilibrium in the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ can be attained from either direction*

7.3 LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

Cato Guldberg and Peter Waage in 1864, long before Haber, were able to describe equilibrium state by a quantitative relation between equilibrium concentration of the reactants and products. In order to appreciate their work better let us consider reaction between gaseous hydrogen and iodine carried out in a sealed vessel at 731 K. The reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

was carried with different initial conditions. In the first four experiments (1, 2, 3 and 4) the sealed reaction vessel contained initially only gaseous hydrogen and gaseous iodine. Each experiment was performed taking different concentrations of hydrogen and/or iodine. After sometimes it was found that intensity of purple colour of the mixture in the sealed vessel became constant and equilibrium was attained. The other two experiments (experiments 5 and 6) were performed taking initially only gaseous HI and thus equilibrium was attained from the opposite direction. Data obtained in all the six sets of experiments are given in Table 7.2.

According to equation

$$\underset{1\ \text{mol}}{H_2(g)} + \underset{1\ \text{mol}}{I_2(g)} \rightleftharpoons \underset{2\ \text{mol}}{2HI(g)}$$

One mole of H_2 reacts with one mole of I_2 to form two moles of HI. It can be seen from the experiments (1-4), that number of moles of H_2 reacted = number of moles I_2 reacted = ½ (number of moles of HI formed).

In experiments 5 and 6, we find that

$$[H_2(g)]_{eq} = [I_2(g)]_{eq}$$

Is there any relationship between the concentrations of the reactants and products at equilibrium. We can try several combinations. Let us consider the simple expression:

$$\frac{[HI(g)]_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$$

It can be seen from Table 7.3 that if we put the equilibrium concentrations of the reactants and products, the above expression is far from

Table 7.2 Initial and Equilibrium Concentrations of H_2, I_2 and HI

Experiment Number	Initial concentration/mol L^{-1}			Equilibrium concentration/mol L^{-1}		
	$[H_2(g)]$	$[I_2(g)]$	$[HI(g)]$	$[H_2(g)]$	$[I_2(g)]$	$[HI(g)]$
1	2.4×10^{-2}	1.38×10^{-2}	0	1.14×10^{-2}	0.12×10^{-2}	2.52×10^{-2}
2	2.4×10^{-2}	1.68×10^{-2}	0	0.92×10^{-2}	0.20×10^{-2}	2.96×10^{-2}
3	2.44×10^{-2}	1.98×10^{-2}	0	0.77×10^{-2}	0.31×10^{-2}	3.34×10^{-2}
4	2.46×10^{-2}	1.76×10^{-2}	0	0.92×10^{-2}	0.22×10^{-2}	3.08×10^{-2}
5	0	0	3.04×10^{-2}	0.345×10^{-2}	0.345×10^{-2}	2.35×10^{-2}
6	0	0	7.58×10^{-2}	0.86×10^{-2}	0.86×10^{-2}	5.86×10^{-2}

constant. However, if we consider the expression,

$$\frac{[HI(g)]^2_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$$

we find that this expression gives constant value (as shown in Table 7.3) in all the six cases. It can be seen that in this expression the power of the concentration for reactants and products are actually the stoichiometric coefficients in the equation for the chemical reaction. The value of this expression at equilibrium is known as the **equilibrium constant** and it is represented by the symbol. K_c. Thus, for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant, K_c is written as

$$K_c = \frac{[HI(g)]^2_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$$

Generally the subscript 'eq' (used for equilibrium) is omitted from the concentration terms. It is taken for granted that the concentrations in the expression for K_c are equilibrium values. We, therefore, write

$$K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

The subscript 'c' indicates that K_c is expressed in concentrations of mol L^{-1}. It may be again emphasized that after the equilibrium is established, the expression

$$\frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

is constant at a given temperature irrespective of the initial concentrations of $H_2(g)$, $I_2(g)$ and HI(g) taken in the closed vessel (Table.7.2 & 7.3).

For all chemical reactions in general, the expression for the equilibrium constant is interrelated to the stoichiometric coefficients of the chemical equation for the reaction and a general statement known as the **Equilibrium Law** or **Law of Chemical Equilibrium** can be enunciated.

At a given temperature, the product of concentrations of the reaction products each raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value.

Thus, the equilibrium constant for a general reaction

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

is expressed as

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The reaction products (C and D) occur in the numerator, and the reactants (A and B) in the denominator. Each concentration (e.g., [C] [D], etc) is raised to a power equal to stoichiometric coefficient in the balanced chemical equation for the reaction. Equilibrium constant for the reaction, $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$, is written as

$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

Molar concentration of different species are indicated by enclosing these in square brackets and it is implied that these are equilibrium concentrations. While writing expression for equilibrium constant, symbol for phases (s, l,

Table 7.3 Expression Involving the Equilibrium Concentration of Reactants
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Experiments	$\frac{[HI(g)]_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$	$\frac{[HI(g)]^2_{eq}}{[H_2(g)]_{eq}[I_2(g)]_{eq}}$
1	1840	46.4
2	1610	47.6
3	1400	46.7
4	1520	46.9
5	1970	46.4
6	790	46.4

g) are ignored unless it is very essential.

Equilibrium constants are normally given for chemical equations written with smallest whole numbers for stoichiometric coefficients. If we change the stoichiometric coefficients in a chemical equation (for example by multiplying throughout by a factor) then we must make sure that the expression for equilibrium constant also reflects that change.

Suppose we write equilibrium constant for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ as

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = x$$

The equilibrium constant for the reverse reaction, $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, at the same temperature is

$$K_c' = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{x} = \frac{1}{K_c}$$

Thus, $K_c' = \dfrac{1}{K_c}$

Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward reaction.

On the other hand, if the above reaction is written as

$\frac{1}{2} H_2(g) + \frac{1}{2} I_2(g) \rightleftharpoons HI(g)$

The equilibrium constant for the above reaction is given by

$$K_c'' = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} = \left[\frac{[HI]^2}{[H_2][I_2]}\right]^{1/2} = x^{1/2} = K_c^{1/2}$$

The equation, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, when multiplied by ½ gives $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$ and the relation between their equilibrium constants are given above. On multiplying the equation by n, we get

$nH_2(g) + nI_2(g) \rightleftharpoons 2nHI(g)$

Therefore, equilibrium constant for the reaction is equal to K_c^n. These findings are summarized in Table 7.4.

Table 7.4 Relations between Equilibrium Constants for a General Reaction and its Multiples

Chemical Equation	Equilibrium Constant
$aA + bB \rightleftharpoons cC + dD$	K
$cC + dD \rightleftharpoons aA + bB$	$K_1\left(=\frac{1}{K}\right)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K_2\left(=K^n\right)$

Equilibrium Constant and its Units

We have already noted that the value of an equilibrium constant has meaning only when we give the corresponding balanced chemical equation. Its value changes for the new equation obtained by multiplying or dividing the original equation by a number. The value for equilibrium constant, K_c is calculated by substituting the concentration in mol/L and for K_p by substituting partial pressure in Pa, kPa, bar or in atm. Thus, units of equilibrium constant will turn out to be units based on molarity or pressure, unless the sum of the exponents in the numerator is equal to the sum of the exponents in the denominator. Thus for the reaction:

$H_2(g) + I_2(g) \rightleftharpoons 2HI$, K_c and K_p do not have any unit

$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3$, K_c has unit $(mol/L)^{-2}$ and K_p has unit bar^{-2} or

$N_2O_4(g) \rightleftharpoons 2\,NO_2$, K_c has unit mol/L and K_p has unit bar

However, these days we express equilibrium constants in dimensionless quantities by specifying the standard state of the reactants and the products. The standard state for pure gas is 1 bar and now the partial pressure are measured with respect to this standard. Thus a pressure of 2 bar in terms of this standard state is equal to 2bar/1bar = 2, a dimensionless number. Similarly for a solute the standard state; c_0, is 1 molar solution and all concentrations are measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Thus in this system both K_p and K_c are dimensionless quantities but have different numerical values due to different standard states. We can specify the height of a building in metre or feet; but if we have a standard height say of 10 ft., then the height of a 30 ft building in terms of standard height is $\dfrac{30\text{ ft}}{10\text{ ft}} = 3$.

7.4 HOMOGENEOUS EQUILIBRIA

In a homogeneous system, all the reactants and products are in the same phase. For example, in the gaseous reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, reactants and products are in the homogeneous gas phase.

Similarly in reactions:

$$CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$$

and $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$

all the reactants and products are in homogeneous solution phase. We shall now consider equilibrium constant for some homogeneous reactions.

7.4.1 Equilibrium Constant in Gaseous Systems

So far we have expressed equilibrium constant of the reactions in terms of molar concentration of the reactants and products, and used symbol, K_c for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of *partial pressure*.

The ideal gas equation (Unit-2) is written as

$$pV = nRT$$

$$\text{or } p = \frac{n}{V}RT$$

Here, p is the pressure in Pa, n is the amount of the gas, V is the volume in m^3 and T is the temperature in kelvin

Therefore, $p = \frac{n}{V}RT$; $\frac{n}{V}$ is in $\frac{\text{mol}}{\text{m}^3}$

If concentration, is in mol / L $= \frac{\text{mol}}{\text{dm}^3}$, and p is in bar then

$p = cRT$,

we can also write $p = [\text{gas}]\,RT$).

Here, $R = 0.0831 \frac{\text{bar litre}}{\text{mol K}}$

At constant temperature, the pressure of the gas is proportional to its concentration, i.e.

$p \propto [\text{gas}]$

For reaction in equilibrium $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, We can write either

$$K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} \text{ or } K_p = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})}$$

Further, since $p_{HI} = [HI(g)]RT$

$$p_{H_2} = [H_2(g)]RT$$

$$p_{I_2} = [I_2(g)]RT$$

Therefore,

$$K_p = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} = \frac{[HI(g)]^2[RT]^2}{[H_2(g)]RT.[I_2(g)]RT}$$

$$= \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} = K_c$$

In this example, $K_p = K_c$ i.e. both equilibrium constants are equal. However, this is not always the case. For example in reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3} = \frac{[NH_3(g)]^2(RT)^2}{[N_2(g)]RT.[H_2(g)]^3(RT)^3}$$

$$= \frac{[NH_3]^2}{[N_2][H_2]^3}(RT)^{-2} = K_c(RT)^{-2} \text{ or } K_p = K_c(RT)^{-2}$$

Similarly, for a general reaction

$$aA + bB \rightleftharpoons cC + dD$$

We can write,

$$K_p = \frac{(p_C^c)(p_D^d)}{(p_A^a)(p_B^b)} = \frac{[C]^c[D]^d(RT)^{c+d}}{[A]^a[B]^b(RT)^{a+b}}$$

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{(c+d)-(a+b)}$$

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{\Delta n} = K_c(RT)^{\Delta n}$$

where Δn = number of moles of products – number of moles of reactants in the balanced chemical equation.

(It is necessary that while calculating the values of K_p, pressure should be expressed in bar as standard state is 1 bar). We have seen in Unit 1,

1 pascal, Pa = $1Nm^{-2}$, and 1 bar = 10^5Pa

K_p values for a few selected reactions are given in Table 7.5.

Table 7.5 Equilibrium Constants, K_p for a Few Selected Reactions

Reaction	Temperature/K	K_p
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$	298	6.8×10^5
	400	41
	500	3.6×10^{-2}
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	298	4.0×10^{24}
	500	8.5×10^{10}
	700	3.0×10^4
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	298	0.98
	400	47.9
	500	1700

It can be seen from the above table that the equilibrium constant changes considerably with temperature.

Example 7.3

For the equilibrium

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$,

the value of the equilibrium constant, K_c is 3.75×10^{-6} at 1069K. Calculate the K_p for reaction at this temperature.

Solution

For the reaction, $\Delta n = (2+1) - 2 = 1$

$K_p = K_c (RT)^{\Delta n}$

$= 3.75\times10^{-6} (0.0831 \times 1069)$

$= 3.33 \times 10^{-2}$

7.5 HETEROGENEOUS EQUILIBRIA

Equilibrium in a system having more than one phase is called *heterogeneous equilibrium*. For example, the equilibrium between water vapour and liquid water in a *closed container* is an example of heterogeneous equilibrium.

$H_2O(l) \rightleftharpoons H_2O(g)$

In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution,

$Ca(OH)_2(s) + (aq) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$

is a heterogeneous equilibrium.

Heterogeneous equilibria often involve *pure solids* or *liquids*. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid as the **molar concentration of a pure solid or liquid is constant, independent of the amount present.** In other words if a substance 'X' is involved, then [X(s)] and [X(l)] are constant, whatever the amount of 'X' is taken. Contrary to this, [X(g)] and [X(aq)] will vary as the amount of X in a given volume varies. Let us take thermal dissociation of calcium carbonate which is an interesting and important example of heterogeneous chemical equilibrium.

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

On the basis of the stoichiometric equation, we can write

$$K_c' = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

Since $[CaCO_3(s)]$ and [CaO(s)] are both constant, therefore modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$K_c = [CO_2(g)]$

or $K_p = p_{CO_2}$

This shows that at a particular temperature, there is a constant concentration or pressure of CO_2 in equilibrium with CaO(s) and $CaCO_3(s)$. Experimentally it has been found that at 1073 K, the pressure of CO_2 in equilibrium with $CaCO_3(s)$ and CaO(s), is 2.5×10^4 Pa. Therefore, equilibrium constant at 1073 K for the above reaction is

$$K_p = p_{CO_2} = \frac{2.5\times10^4\ Pa}{p^0} = \frac{2.5\times10^4\ Pa}{10^5\ Pa} = 0.25$$

The molar concentration of a substance is measured by dividing the number of moles of the substance by the volume it occupies. However, moles divided by volume is proportional to mass divided by volume or density of the substance. Because density is an *intensive property*, it follows that molar concentration of a pure solid or liquid always has the same value, no matter how much or how little of the substance is

present in the system at a given temperature. Mathematically,

$$\text{molar concentration} \propto \frac{\text{mass}}{\text{volume}} = \text{density}$$

Similarly, in the equilibrium between nickel, carbon monoxide and nickel carbonyl (used in the purification of nickel),

$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$,

The equilibrium constant is written as

$$K_c = \frac{[Ni(CO)_4]}{[CO]^4}$$

It must be remembered that *pure substances must be present (however small it may be) for the equilibrium to exist, but their concentrations or partial pressure do not appear in the expression of the equilibrium constant.* Thus, in normal course, pure liquid and solids are ignored while writing expression for equilibrium constants. In the reaction,

$Ag_2O(s) + 2HNO_3(aq) \rightleftharpoons 2AgNO_3(aq) + H_2O(l)$

the equilibrium constant can be written as

$$K_c = \frac{[AgNO_3]^2}{[HNO_3]^2}$$

7.6 APPLICATION OF EQUILIBRIUM CONSTANTS

Before we consider the applications of equilibrium constants, let us consider its important features:

1. The expression for equilibrium constant, K is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.
2. The value of equilibrium constant is independent of initial concentration of the reactants and products. Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature. The value of course varies with temperature.
3. The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.
4. The equilibrium constant, K for a reaction is related to the equilibrium constant of the corresponding reaction whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

Now we will consider some applications of equilibrium constant and use it to answer questions like:

- predicting the extent of a reaction on the basis of its magnitude,
- predicting the direction of the reaction, and
- calculating equilibrium concentrations.

7.6.1 Predicting the Extent of a Reaction

The magnitude of equilibrium constant is very useful especially in reactions of industrial importance. An equilibrium constant tells us whether we can expect a reaction mixture to contain a high or low concentration of product(s) at equilibrium. (It is important to note that an equilibrium constant tells us nothing about the rate at which equilibrium is reached). In the expression of K_c or K_p, product of the concentrations of products is written in numerator and the product of the concentrations of reactants is written in denominator. High value of equilibrium constant indicates that product(s) concentration is high and its low value indicates that concentration of the product(s) in equilibrium mixture is low.

For reaction, $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$, the value of

$$K_p = \frac{(p_{HBr})^2}{(p_{H_2})(p_{Br_2})} = 5.4 \times 10^{18}$$

The large value of equilibrium constant indicates that concentration of the product, HBr is very high and reaction goes nearly to completion.

Similarly, equilibrium constant for the reaction $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ at 300 K is very high and reaction goes virtually to completion.

$$K_c = \frac{[HCl]^2}{[H_2][Cl_2]} = 4.0 \times 10^{31}$$

Thus, large values of K_p or K_c (larger than about 10^3), favour the products strongly. For intermediate values of K (approximately in the

range of 10^{-3} to 10^{3}), the concentrations of reactants and products are comparable. Small values of equilibrium constant (smaller than 10^{-3}), favours the reactants strongly.

At 298K, for reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 4.8\times10^{-31}$$

The very small value of K_c implies that reactants N_2 and O_2 will be the predominant species in the reaction mixture at equilibrium.

7.6.2 Predicting the Direction of the Reaction

The equilibrium constant is also used to find in which direction an arbitrary reaction mixture of reactants and products will proceed. For this purpose, we calculate the **reaction quotient**, Q. The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give Q_c, or with partial pressures to give Q_p) at any stage of reaction. For a general reaction:

$aA + bB \rightleftharpoons cC + dD$

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Then, if $Q_c > K_c$, the reaction will proceed in the direction of reactants(reverse reaction) .

if $Q_c < K_c$, the reaction will move in the direction of the products

if $Q_c = K_c$, the reaction mixture is already at equilibrium.

In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, if the molar concentrations of H_2, I_2 and HI are 0.1 mol L^{-1}, 0.2 mol L^{-1}, and 0.4 mol L^{-1} respectively at 783K, then reaction quotient at this stage of the reaction is

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

K_c for this reaction at 783 K is 46 and we find that $Q_c < K_c$. The reaction, therefore, will move to right i.e. more $H_2(g)$ and $I_2(g)$ will react to form more HI (g) and their concentration will decrease till $Q_c = K_c$.

Example 7.4

A mixture of H_2, N_2 and NH_3 with molar concentrations 3.0×10^{-3} mol L^{-1}, 1.0×10^{-3} mol L^{-1} and 2.0×10^{-3} mol L^{-1} respectively was prepared at 500 K. At this temperature, the value of K_c for reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, is 61. Predict whether at this stage the concentration of NH_3 will increase or decrease.

Solution

Reaction quotient, Q_c for the reaction will be written as

$$Q_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} = \frac{(2.0\times10^{-3})^2}{(1.0\times10^{-3})(3.0\times10^{-3})^3}$$

$$= \frac{4.0\times10^{-6}}{27.0\times10^{-12}} = 0.149\times10^{6} \cong 1.5\times10^{5}$$

Since $Q_c > K_c$, reaction will go in the left direction and ammonia will decompose into hydrogen and nitrogen.

7.6.3 Calculating Equilibrium Concentrations

Once the value of the equilibrium constant for a reaction is known, we can use it to calculate the concentration of a substance (reactant or product) in the equilibrium mixture.

Example 7.5

The reaction,

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

is at equilibrium at 1300K in a one litre flask. The gaseous equilibrium mixture contains 0.30 mol of CO, 0.10 mol of H_2 and 0.020 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

Solution

The equilibrium constant for the reaction,

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ is written as

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

Now substituting the values of known concentrations and K_c.

$$3.90 = \frac{[CH_4](0.020)}{(0.30)(0.10)^3}$$

$$\text{or} \quad \frac{[CH_4]}{c_o} = \frac{(3.90)(0.30)(0.10)^3}{(0.020)} = 0.059$$

(c_o = 1M is the standard state)

and therefore, $[CH_4]$ = 0.059 M

Example 7.6

Phosphorus pentachloride decomposes according to the reaction

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

1.50 mol of PCl_5 is placed in a 500 mL closed reaction vessel and allowed to reach equilibrium with its decomposition products, phosphorus trichloride and chlorine at 523 K. Equilibrium constant, K_c is 1.80. What is the composition of the mixture at equilibrium?

Solution

For the reaction

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

The initial molar concentration of

$$PCl_5 = \frac{1.50 \text{ mol}}{0.500\text{L}} = 3.00 \text{ mol L}^{-1}$$

Suppose change in molar concentration of PCl_5 is(– x) mol L^{-1}

Then,

	PCl_5	PCl_3	Cl_2
Initial molar concentration	3.00	0	0
Change in molar concentration	$-x$	$+x$	$+x$
Equilibrium molar concentration	$(3.00-x)$	x	x

Now substituting the value of equilibrium concentrations in the expression for equilibrium constant, we get

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{x \times x}{(3.00 - x)}$$

or $x^2 + 1.80\,x - 5.40 = 0$

Therefore,

$$x = \frac{-1.80 \pm \sqrt{(1.80)^2 - 4(1)(-5.40)}}{2}$$

$$= 1.59 \text{ and } -3.39$$

Since concentration must be positive, therefore, 1.59 mol L^{-1} is selected as appropriate solution. Therefore, equilibrium concentration of $[PCl_5]$ = (3.00 – 1.59) mol L^{-1} = 1.41 mol L^{-1} and

$[PCl_3]$ = 1.59 mol L^{-1}

$[Cl_2]$ = 1.59 mol L^{-1}

7.7 FACTORS AFFECTING EQUILIBRIA

K_c is appropriately the equilibrium constant because it has the same value regardless of the amounts of the reactants and products that are put into the system. In other words, K_c is independent of initial concentrations. However, if a system at equilibrium is subjected to a change in the concentration of one or more of the reacting substances, then the system is no longer at equilibrium; and net reaction takes place in some direction until the system returns to equilibrium once again. We have already learnt about effect of temperature on phase equilibria and solubility of solids. We noted, for example, that an increase in temperature leads to change in the solubility. We have already seen, how, at a given temperature we can calculate the concentrations of the reactants and products at equilibrium for any initial concentration if we know the value of equilibrium constant. Even if we do not know how equilibrium constant changes with temperature, we can make a *qualitative prediction* about the effect of a change in conditions on an equilibrium by using *Le Chatelier's principle*. It states that a **change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner as to reduce or to counteract the effect of the change.** *This is applicable to all physical and chemical equilibria.* In the following sub-sections, we shall discuss the effect of concentration, pressure, temperature and catalyst on equilibria.

7.7.1 Effect of Concentration Change

We can restate the Le Chatelier's principle for the special case of the concentration changes. *'When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium*

mixture changes so as to minimize the effect of concentration change'.

Let us take the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

If we add H_2 at equilibrium, the concentration of H_2 is increased and it is no longer its equilibrium concentration. According to Le Chatelier's principle, a new equilibrium will be set up in which concentration of H_2 should be less than it was after the addition of H_2 but more than what it was in the original mixture. The adjustment of equilibrium never fully compensates for the change in the concentration that was made. Here equilibrium will shift in a direction, which can consume hydrogen. This is only possible when more of H_2 and I_2 react and form HI resulting in shift of equilibrium in right (forward) direction (Fig.7.7).

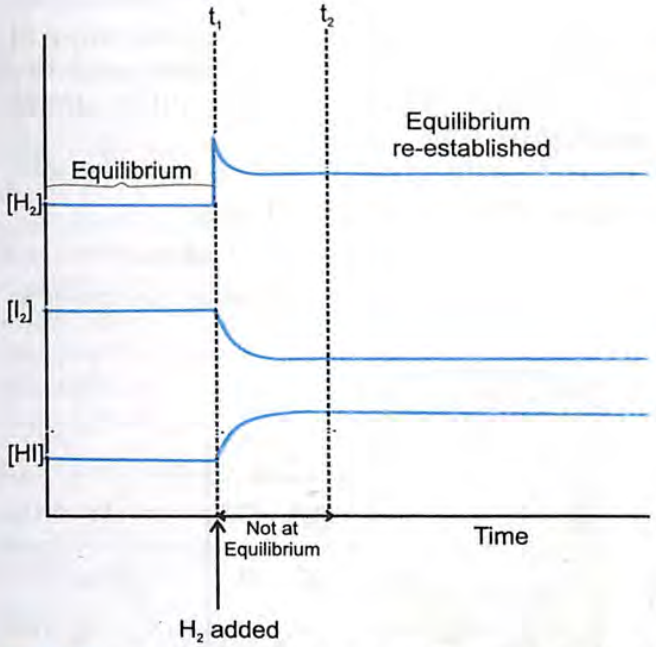


Fig.7.7 *Effect of addition of H_2 on change of concentration for the reactants and products in the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$*

We can arrive at the same conclusion by considering the reaction, quotient

$$Q_c = \frac{[HI]^2}{[H_2][I_2]}$$

If hydrogen is added at equilibrium, $[H_2]$ increases and Q_c becomes less than K_c. Reaction, therefore, moves in the forward direction i.e. $[H_2]$ and $[I_2]$ decrease and [HI] increases until $Q_c = K_c$ and equilibrium is re-established. Removal of a product often has a great importance in industrial processes. When a product is removed, a reaction that would otherwise come to equilibrium without going to completion, can be driven in the forward direction. Removal is feasible when one of the products is a gas or a substance that can be easily vaporized. In case of ammonia manufacturing, ammonia is liquefied and removed from the reaction mixture and reaction moves in the forward direction. Similarly in a large scale production of CaO (used as important material in building industry) from $CaCO_3$, constant removal of CO_2 from the kiln drives the reaction to completion. It should be remembered that continuous removal of a product maintains Q_c at a value less than K_c and reaction continues to move in the forward direction.

Effect of Concentration – An experiment

This can be demonstrated by the following well known reaction

$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$;

Yellow Colourless Deep red

$$K_c = \frac{[FeSCN^{2+}(aq)]}{[Fe^{3+}(aq)][SCN^-(aq)]}$$

Let us prepare two solutions (i) 100 mL of 0.002 mol L^{-1} of potassium thiocyanate and (ii) 150 mL of 0.20 mol L^{-1} of iron (III) nitrate and note their colours. Now take 10 mL of iron (III) nitrate solution in a test tube and add two drops of potassium thiocyanate solution. After shaking the test tube, colour of the solution turns reddish. This colour is due to formation of $FeSCN^{2+}$. After the equilibrium is attained, and intensity of the colour becomes constant, add two more drops of potassium thiocyanate solution and see the change thereafter in colour. Addition of potassium thiocyanate increases the concentration of SCN^- ions, and therefore, equilibrium shifts to right and colour intensity of solution increases.

7.7.2 Effect of Pressure Change

A pressure change obtained by changing the volume can affect the yield of products in a gaseous reaction. This happens only when total

number of moles of gaseous reactants and total number of moles of gaseous products are different in the chemical equation for the reaction. In methanation reaction

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

4 mol of reactant gases ($CO + 3H_2$) become 2 mol of product gases ($CH_4 + H_2O$).

Suppose equilibrium mixture (for above reaction) kept in a cylinder fitted with a piston at constant temperature is compressed to one half of its original volume. Then, total pressure will be doubled (according to pV = constant). The partial pressure and therefore, concentration of reactants and products have changed and the mixture is no longer at equilibrium. The direction in which the reaction goes to re-establish equilibrium can be predicted by applying the Le Chatelier's principle. Since pressure has doubled, the equilibrium now shifts in forward direction, a direction in which the number moles of the gas or pressure decreases (we know pressure is proportional to moles of the gas) (Fig.7.8). This can be understood by using reaction quotient, Q_c. Let [CO], $[H_2]$, $[CH_4]$ and $[H_2O]$ be the molar concentrations at equilibrium for methanation reaction. When volume of the reaction mixture is halved, the partial pressure and the concentration are doubled. We obtain the reaction quotient by replacing each equilibrium concentration by double its value,

$$Q_c = \frac{\left(2[CH_4]\right)\left(2[H_2O]\right)}{(2[CO])\left(2[H_2]\right)^3} = \frac{4}{16}\frac{[CH_4][H_2O]}{[CO][H_2]} = \frac{K_c}{4}$$

As $Q_c < K_c$, the reaction proceeds in the forward direction.

For deciding the direction of the reaction when the pressure of the reaction mixture is increased, we generally ignore liquid and solid reactants or products. They are not affected much by pressure changes. In reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, when pressure is increased, the reaction goes in the reverse direction because number of moles of gas increases in the forward direction.

7.7.3 Effect of Temperature Change

Temperature affects a reaction in two ways: (i) It increases rates of reactions and the equilibrium is reached sooner (ii) It affects equilibrium constant, K.

For methanation reaction which is exothermic,

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$;

$\Delta_r H^\ominus = -206.2 \text{ kJ mol}^{-1}$

the values of equilibrium constant are given at

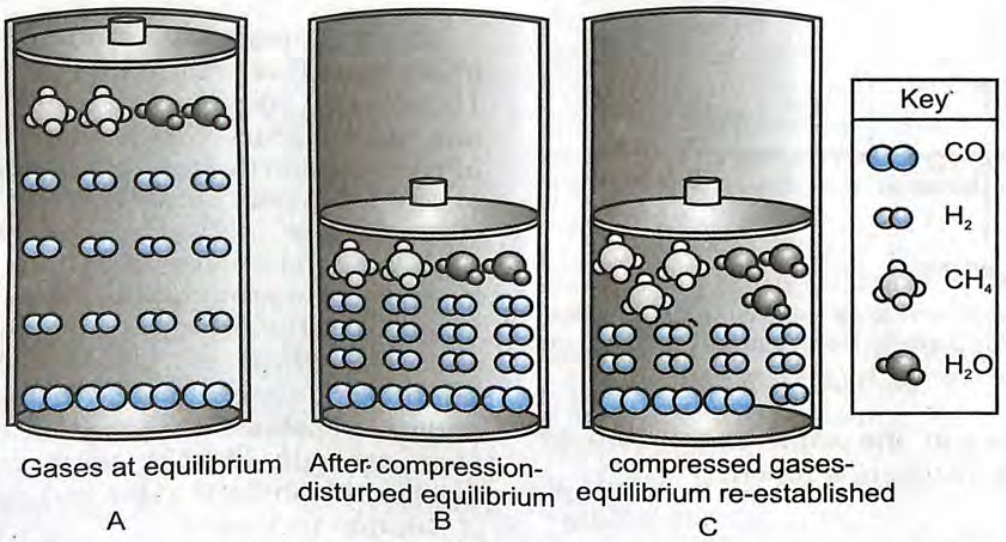


Fig.7.8 *Effect of pressure on equilibrium in methanation reaction. The approximate composition is represented by the proportion of different molecules. Actual arrangement of molecules in a gas is random. (A) original equilibrium mixture of CO, H_2, CH_4 and H_2O molecules (B) The gases are compressed for one half of their initial volume, increasing their partial pressure so that mixture is no longer at equilibrium (C) Equilibrium is re-established when the reaction goes in the forward direction $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$. In this way, total number of molecules is reduced which reduces the initial pressure increase.*

different temperature in (Table 7.6). The way, the temperature affects K_c or K_p depends on enthalpy change, $\Delta_r H$, of the reaction. **An increase in temperature always shifts the equilibrium position in endothermic direction, and decrease in temperature always shifts the equilibrium position in the exothermic direction.**

Table 7.6 Equilibrium Constant for Methanation at Different Temperature

Temperature/K	K_c
298	4.9×10^{27}
800	1.38×10^{5}
1000	2.54×10^{2}
1200	3.92

Production of ammonia according to the reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta_r H^\ominus = -92.38$ kJ mol^{-1}

is an exothermic process. According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favourable for high yield of ammonia. In practice, very low temperature cannot be used because reaction is then too slow.

Effect of Temperature – An Experiment

Effect of temperature on equilibrium can be demonstrated by taking NO_2 gas which dimerizes into N_2O_4.

$2NO_2(g) \rightleftharpoons N_2O_4(g)$; $\Delta_r H^\ominus = -57.2$ kJ mol^{-1}

We can prepare NO_2 gas by adding Cu turnings to conc. HNO_3 and collect the gas through a delivery tube in the two test tubes each of 5 mL. Ensure equal intensity of the colour of the gas in each test tube and seal the stopper of the tube using araldite. Now take three 250 mL beakers and number them as 1, 2 and 3. Beaker number 1 is filled with freezing mixture; beaker number 2, with water at room temperature and beaker number 3 with hot water (temperature 363K). When both the test tubes are kept in beaker number 2, intensity of brown colour of the gas is almost equal. After keeping the test tubes for about 8 to 10 minutes in water maintained at room temperature, remove them and place one in beaker No.1 (contains freezing mixture) and other in beaker No.3 (contains hot water). You will observe that in beaker No.1 intensity of colour decreases whereas in beaker No.3 intensity of colour increases. It is easy to understand the reason for this observation. At low temperature, N_2O_4 is favoured which is a colourless gas and at higher temperature NO_2 is favoured which is a brown gas.

Effect of temperature can also be demonstrated for another endothermic reaction

$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$

At room temperature, the equilibrium mixture is blue due to $CoCl_4^{2-}$. When cooled in a freezing mixture, the colour of the mixture turns pink due to $Co(H_2O)_6^{2+}$.

7.7.4 Effect of a Catalyst

A catalyst does not affect equilibrium constant. It increases the rate of both the reactions (forward and reverse) and allows a reaction to reach an equilibrium position more rapidly. It is also important to mention that a catalyst has no effect on the equilibrium composition of a reaction mixture. Conversion of SO_2 into SO_3 is industrially very important in the manufacture of H_2SO_4 by *contact process*.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $K_c = 1.7 \times 10^{26}$

According to the magnitude of the equilibrium constant, reaction should go to almost completion but oxidation of SO_2 to SO_3 is so slow that it does not give a significant amount of product even after keeping the reactant SO_2 in contact with O_2 for a long time. In presence of platinum or divanadium penta-oxide (V_2O_5) as catalyst, rate of reaction becomes quite appreciable. However, if a reaction has an exceedingly small equilibrium constant, a catalyst would be of little help.

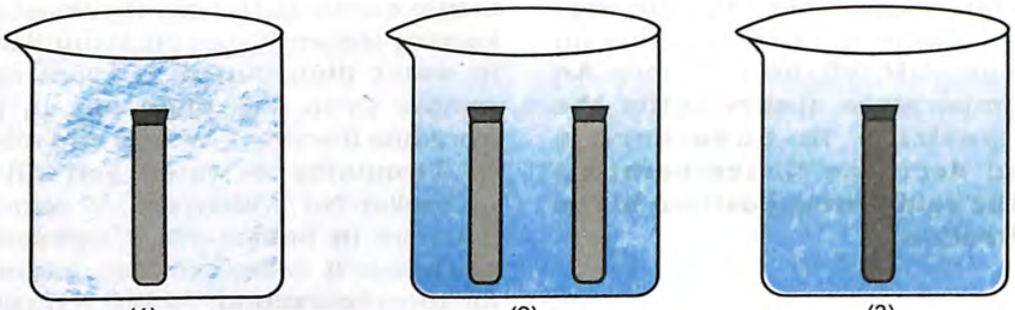


Fig.7.9 *Effect of temperature on equilibrium for the reaction,* $2NO_2(g) \rightleftharpoons N_2O_4(g)$

SUMMARY

Most of the chemical reactions do not go to completion in a closed system and attain a state of equilibrium. Equilibrium is said to have reached in a physical or in a chemical system when rates of forward and reverse processes are equal. At equilibrium, macroscopic properties (such as concentration, pressure) become constant at a constant temperature and state of chemical equilibrium is characterized by its **equilibrium constant**. Equilibrium constant can be expressed in terms of equilibrium concentration of reactants and products. It has a constant value at a fixed temperature. For a general reaction, $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant is written as

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}.$$

This expression is also called the *law of chemical equilibrium.* Pure liquids and solids are ignored in writing the expression for equilibrium constant. In gaseous reaction, concentration is sometimes replaced by partial pressure, and K_c, is replaced by K_p. K_c and K_p are related by the expression $K_p = K_c (RT)^{\Delta n}$, where Δn is the difference between the total number of moles of gaseous products and reactants. When K_c is very large, the equilibrium mixture has mostly products and when K_c is very small, the equilibrium mixture has mostly reactants.

Reaction quotient, Q_c has the form of equilibrium constant expression and is equal to K_c at equilibrium. By substituting the concentration of all the substances in the reaction mixture in the expression for Q_c, direction of the reaction can be predicted. The composition of the reaction mixture can be calculated starting from various initial concentrations, if the value of K_c is known. Concentration, pressure and temperature including catalyst are very important and yield of the product can be controlled by controlling these factors. Removing a product from the reaction mixture shifts the equilibrium composition to give more products. Le Chatelier's principle is useful in providing the effect of such changes. *It states that a change in any of the factors that determine the equilibrium conditions of a system will cause system to change in such a manner as to reduce or to counteract the effect of the change.*

EXERCISES

7.1 A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased
(a) What is the initial effect of the change on vapour pressure?
(b) How do rates of evaporation and condensation change initially?
(c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

7.2 Fill in the blanks in the following table which lists the solubility data of oxygen in water at 299K.

O_2 pressure/(kPa)	$[O_2(g)]_{eq}$/molL^{-1}	$[O_2(aq)_{eq}]$ / mol L^{-1}	$\frac{[O_2(aq)]_{eq}}{[O_2(g)]_{eq}}$
106.4	-	0.012	-
-	0.080	-	0.029
333.3	0.13	-	0.029
466.1	-	0.0053	-
598.8	-	-	0.028

7.3 At a certain temperature and a total pressure of 10^5 Pa, iodine vapour contains 40% by volume of I atoms

$I_2(g) \rightleftharpoons 2I(g)$

Calculate K_p for the equilibrium.

7.4 Which of the following reactions involve homogeneous equilibria and which involve heterogeneous equibria?

(a) $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$

(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

(c) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(d) $CH_3COOC_2H_5(aq) + H_2O(1) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

(e) $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

7.5 Write the expression for the equilibrium constant, K for each of the following reactions,

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

(ii) $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

(iii) $I_2(s) + 5F_2(g) \rightleftharpoons 2IF_5(g)$

(iv) $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

(v) $Na_2CO_3(s) + SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons Na_2SO_4(s) + CO_2(g)$

(vi) $PbI_2(s)+aq \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

7.6 For the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

At 400 K, $K_p = 41$. Find the value of K_p for each of the following reactions at the same temperature:

(i) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

(ii) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

(iii) $2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$

7.7 Find out the value of K_c for each of the following equilibria from the value of K_p
(a) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, $K_p = 1.8\times10^{-2}$ at 500K
(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_p = 167$ at 1073K

7.8 Explain why pure liquids and solids can be ignored while writing the quilibrium constant expression.

7.9 What qualitative information can you obtain from the magnitude of equilibrium constant?

7.10 Reaction between nitrogen and oxygen takes place as following:

$2N_2(g) + O_2 \rightleftharpoons 2N_2O(g)$

If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a reaction vessel of volume 10 L and allowed to form N_2O at a temperature for which $K_c = 2.0\times10^{-37}$. Determine the composition of equilibrium mixture.

7.11 Nitric oxide reacts with bromine and gives nitrosyl-bromide as per reaction given below

$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$

when 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of nitric oxide and bromine.

7.12 The equilibrium constant expression for a gas reaction is

$$K_c = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

7.13 One mole of H_2O and one mole of CO are taken in a 10 litre vessel and heated to 725 K. At equilibrium 40 per cent of water (by mass) reacts with carbon monoxide according to the equation

$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$

Calculate the equilibrium constant for the reaction.

7.14 At 700 K equilibrium constant for the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

is 54.8. If 0.5 mol L^{-1} of HI(g) is present at equilibrium at 700K, what are the concentrations of $H_2(g)$ and $I_2(g)$ assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700 K.

7.15 The ester, ethyl acetate is formed by the reaction between ethanol and acetic acid and equilibrium is represented as

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$

(i) Write the concentration ratio (reaction quotient), Q_c, for this reaction. Note that water is not in excess and is not a solvent in this reaction.
(ii) At 293K, if one starts with 1.00 mol of acetic acid and 0.180 of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant .
(iii) Starting with 0.500 mol of ethanol and 1.000 mol of acetic acid and maintaining it at 293K, 0.214 mol of ethyl acetate is found after some time. Has equilibrium been reached?

7.16 A sample of pure PCl_5 was introduced into an evacuated vessel at 473K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

7.17 In reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$; $\Delta_r H^\ominus = -92.0$ kJ mol^{-1}
Concentration of hydrogen, carbon monoxide and methanol become constant at equilibrium. What will happen if

(i) volume of the reaction vessel in which reactants and products are contained is suddenly reduced to half.
(ii) the partial pressure of hydrogen is suddenly doubled
(iii) an inert gas is added to the system.

7.18 Hydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction.

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$;

(a) Write an expression for K_p for the above reaction.
(b) How will the value of K_p and composition of equilibrium mixture be affected by
(i) increasing the pressure
(ii) increasing the temperature
(iii) using a catalyst

7.19 At 473K, equilibrium constant, K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as

$PCl_5(s) \rightleftharpoons PCl_3(g) + Cl_2(g)$; $\Delta_r H^\ominus = 124.0$ kJ mol^{-1}

(a) Write an expression for K_c for the reaction
(b) What is the value of K_c for the reverse reaction at the same temperature?
(c) What would be the effect on K_c if (i) more PCl_5 is added (ii) the pressure is increased (iii) the temperature is increased?

7.20 The equilibrium constant for the following reaction is 1.6×10^5 at 1024K.

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024K.

7.21 Which of the following reactions will get affected by increase of pressure? Also mention, whether change will cause the reaction to go into the right or left direction?

(i) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$

(ii) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

(iii) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

(iv) $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$

7.22 For the reaction, $CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$, at 1173K, the magnitude of the equilibrium constant, K_c is 3.6. For each of the following composition, decide whether reaction mixture is at equilibrium. If it is not, decide to which direction the reaction should go

(i) $[CH_4] = 1.07M$, $[H_2S] = 1.20M$, $[CS_2] = 0.90M$, $[H_2] = 1.78M$
(ii) $[CH_4] = 1.45M$, $[H_2S] = 1.29M$, $[CS_2] = 1.25M$, $[H_2] = 1.75M$

7.23 At 1127K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass

$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

Calculate K_c for this reaction at the above temperature.

7.24 Equilibrium constant, K_c for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500K is 0.061. At a particular time, the analysis shows that composition of the reaction mixture is 3.00 mol L^{-1} N_2, 2.00 mol L^{-1} H_2, and 0.500 mol L^{-1} NH_3. Is the reaction at equilibrium? If not, in which direction does the reaction tend to proceed to reach equilibrium?

7.25 Bromine monochloride, BrCl, decomposes into bromine and chlorine and reaches the equilibrium

$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$

for which $K_c = 32$ at 500K. If initially pure BrCl is present at a concentration of 3.30×10^{-3} mol L^{-1}; what is its molar concentration in the mixture at equilibrium?

UNIT 8

EQUILIBRIUM - II
IONIC EQUILIBRIUM IN SOLUTIONS

Objectives

After studying this Unit, you will be able to

- define acids and bases according to Arrhenius, Brönsted-Lowry and Lewis Concepts.
- describe strong and weak acids and bases and their ionization equilibria in terms of ionization constants of acids(K_a) and of bases(K_b).
- explain how degree of ionization depends on concentration of the electrolyte and that of the common ion.
- describe the pH scale for the concentration of hydrogen ion and its extension to other species and quantities.
- explain the ionization of water and its dual role as an acid and a base.
- describe ionic product (K_w) and pK_w for water.
- discuss hydrolysis of salts of weak acid-strong base, strong acid-weak base, and weak acid-weak base.
- understand the principle underlying the titration between acids and bases using indicators.
- describe buffer solutions and explain their preparation and importance.
- justify solubility equilibria of sparingly soluble salts and calculate solubility product constant.

IONIC EQUILIBRIUM IN SOLUTIONS

We know very well that an aqueous solution of sugar does not conduct electricity. However, an aqueous solution of common salt conducts electricity and its conductance increases with increasing concentration of the salt. On this basis, Michael Faraday, in 1824, classified substances into electrolytes and non-electrolytes. The former conduct electricity through their aqueous solutions, the latter do not.

Faraday further classified electrolytes into weak and strong categories depending on the ease with which the electricity is conducted through their aqueous solutions. For example sodium chloride is a strong electrolyte while acetic acid is a weak electrolyte. Svante Arrhenius(1859-1927) explained in 1880 that electrolytes on dissolution produce positive and negative ions which act as the carriers of electricity. The strong electrolytes are completely dissociated into ions while there is incomplete ionization for the weak electrolytes. Equilibrium is established between the ions and the unionized solute molecules in weak electrolytes. We have already learnt about chemical equilibrium in Unit - 7 and shall now apply these concepts to different types of equilibria involving ions in aqueous solutions. Acids, bases and salts (ionic compounds) are electrolytes. Some of these are strong electrolytes while others behave as weak electrolytes.

8.1 ACIDS, BASES AND SALTS

We use acids, bases and salts quite commonly in our daily life. Acetic acid is the main constituent of vinegar beside water; citric acid is found in lemon and orange juices, tartaric acid is found in tamarind paste. All these substances taste sour. Acid comes from the Latin word 'acidus' meaning 'sour' or having a sharp taste. We already know from earlier classes that acids turn blue litmus paper into red and also liberate hydrogen on reaction with certain metals. The commonly used household bases include washing soda and

Michael Faraday (1791-1867)

Faraday was born near London into a family of very limited means. At the age of 14 he was an apprentice to a kind bookbinder who allowed Faraday to read the books he was binding. Through a fortunate chance he became laboratory assistant to Davy, and during 1813-14, Faraday accompanied him to the Continent. During this trip he gained much from the experience of coming into contact with many of the leading scientists of the time. In 1825, he succeeded Davy as Director of the Royal Institution laboratories, and in 1833 he also became the first Fullerian Professor of Chemistry.

Faraday's first important work was on analytical chemistry. After 1821 much of his work was on electricity and magnetism and different electromagnetic phenomena. His ideas have led to the establishment of modern field theory. He discovered his two laws of electrolysis in 1834.

Faraday was a very modest and kind hearted person. He declined all honours and avoided scientific controversies. He preferred to work alone and never had any assistant. He disseminated science in a variety of ways including his Friday evening discourses, which he founded at the Royal Institution. He has been very famous for his Christmas lecture on the 'Chemical History of a Candle'. He published nearly 450 scientific papers.

ammonia solution used for cleaning window panes. These taste bitter and turn red litmus paper into blue. Sodium chloride (common salt) is an important component of our diet and is formed by reaction between hydrochloric acid and sodium hydroxide. Sodium chloride in the solid state exists as a collection of positively charged sodium ions (cations) and negatively charged chloride ions (anions) which are held very strongly by the *Coulombic forces of attraction between oppositely charged ions* (Fig. 8.1). These forces are inversely proportional to the dielectric constant of the medium. In water whose dielectric constant is 80, these forces are reduced by a factor of about 80 in aqueous solutions and ions are free to move. The ions are further stabilized by their hydration with water molecules.

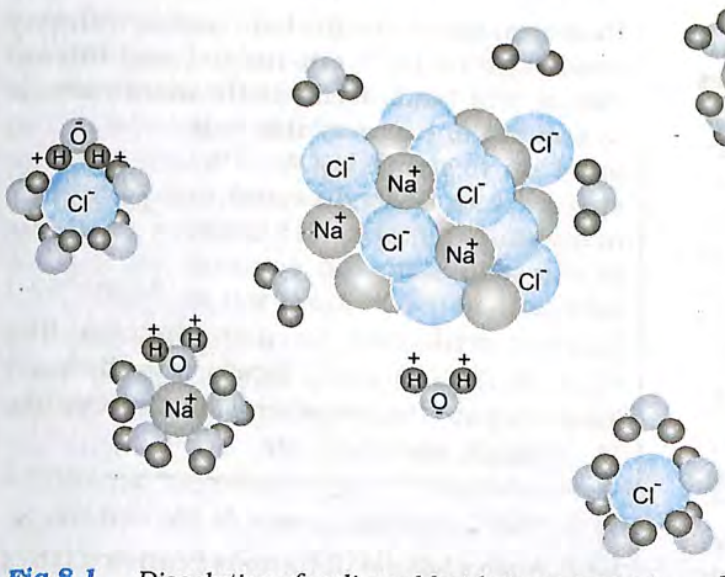


Fig.8.1 *Dissolution of sodium chloride in water. Na^+ and Cl^- ions are stablized by their hydration with polar water molecules.*

It is found that sodium chloride is almost completely dissociated into sodium and chloride ions in its aqueous solution. On the other hand polar molecules, HCl and CH_3COOH, are neutral molecules. These ionize into hydrogen ion and their respective anions in the presence of water. The degree of ionization depends on the polarity and the strength of the bond and the extent of solvation of the ions produced. The terms,

Arrhenius was born near Uppsala, Sweden. He presented his thesis, on the conductivities of electrolyte solutions, to the University of Uppsala in 1884. For the next five years he travelled extensively and visited a number of research centers in Europe. In 1895 he was appointed professor of physics at the newly formed University of Stockholm, serving its rector from 1897 to 1902. From 1905 until his death he was Director of physical chemistry at the Nobel Institute in Stockholm. He continued to work for many years on electrolytic solutions. In 1899 he discussed the temperature dependence of reaction rates on the basis of an equation, now usually known as Arrhenius equation.

He worked in a variety of fields, and made important contributions to immunochemistry, cosmology, the origin of life, and the causes of ice age. He was the first to discuss the 'green house effect' calling by that name. He received Nobel Prize in Chemistry in 1903 for his theory of electrolytic dissociation and its use in the development of chemistry.

Svante Arrhenius (1859-1927)

dissociation and ionization have earlier been used with different meaning. Dissociation refers to the process of separation of ions in water already existing as such in the solid state of the solute as in sodium chloride while ionization corresponds to a process in which a neutral molecule splits into charged ions in the solution. Here, we shall not distinguish between the two and use the two terms interchangeably.

8.1.1 Arrhenius Acids and Bases

Arrhenius defined acids as substances that produce hydrogen ions in water and bases that produce hydroxyl ions. Thus according to Arrhenius the acidic properties of a substance in aqueous solution are due to the presence of the hydrogen ion H^+ (aq) and the basic properties of a substance in aqueous solution are due to the presence of the hydroxyl ion OH^-(aq). Thus the ionization of an acid HX in water can be represented by either of the following equations:

$$HX(aq) \rightarrow H^+(aq) + X^-(aq) \qquad (8.1)$$

or

$$HX(aq) + H_2O(l) \rightarrow H_3O^+(aq) + X^-(aq) \qquad (8.2)$$

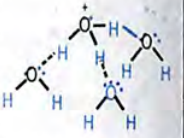
The ion H_3O^+ is known as **hydronium ion** (see box). We use both H^+ (aq) and H_3O^+ (aq) to represent the hydrated hydrogen ion as a proton surrounded by water molecules. In this book, it ordinarily will be represented by H^+(aq). Similarly a base molecule like MOH ionizes in aqueous solution according to the equation:

$$MOH(aq) \rightarrow M^+(aq) + OH^-(aq) \qquad (8.3)$$

The hydroxyl ion also exists in the hydrated form in the aqueous solution (see box). The acids and bases defined in this way are called as *Arrhenius acids and bases.*

Hydronium and Hydroxyl Ions

Hydrogen ion by itself a bare proton with very small size (~ 10^{-13} cm radius) and intense electric field, binds itself with the water molecule at one of the two available lone pairs on it giving H_3O^+. This species has been detected in many compounds (e.g. $H_3O^+Cl^-$) in the solid state. In aqueous solution the hydronium ion is further hydrated to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. Similarly the hydroxyl ion is hydrated to give several ionic species like $H_3O_2^-$, $H_5O_3^-$ and $H_7O_4^-$ etc.



$H_9O_4^+$ ion in $HBr.4H_2O$

8.1.2 The Brönsted-Lowry Acids and Bases

The Danish chemist Johannes Brönsted (1874-1936) and the English chemist, Thomas M. Lowry (1874-1936) gave a more general definition of

acids and bases. They proposed independently in 1923 that the *acids are substances that are capable of donating a proton and the bases are substances capable of accepting a proton.* Accordingly HCl is an acid as it is capable of donating a proton when it is dissolved in water. It donates its proton to H_2O molecule that acts as a base. The same concept of proton transfer is applicable even in a nonaqueous medium. Thus the reaction between HCl and NH_3 in the gas phase can be represented by the equation:

$$HCl(g) + NH_3(g) \rightarrow NH_4^+(g) + Cl^-(g) \qquad (8.4)$$

Here HCl, a Brönsted acid, transfers its proton to NH_3 molecule that acts as a Brönsted base by accepting the proton. But according to Arrhenius for NH_3 to act as a base it should have produced a hydroxyl ion. For the sake of clarification between the Arrhenius and Bronsted-Lowry definitions of acids and bases let us consider the reaction:

adds proton

$$\underset{\text{base}}{NH_3(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{NH_4^+(aq)} + \underset{\text{conjugate base}}{OH^-(aq)} \qquad (8.5)$$

loses proton

In the above equation water acts as a Brönsted acid as it donates a proton to ammonia molecule that acts as a Brönsted base. Also, the solution is basic according to Arrhenius, as hydroxyl ion is produced. It can be seen that in equation (8.5), a proton transfer takes place both in the forward and the reverse reactions. In the forward reaction as mentioned earlier water molecule acts as a proton donor and ammonia molecule as proton acceptor thus acting as Brönsted acid and Brönsted base respectively. In the reverse reaction proton is transferred from NH_4^+ to OH^-. Here NH_4^+ acts as a Brönsted acid while OH^- acts as a Brönsted base. The pair of an acid and a base like H_2O and OH^- or NH_4^+ and NH_3, which differ by the presence or absence of a proton are called **conjugate acid-base pair.** Thus OH^- is the conjugate base of H_2O and NH_4^+ is the conjugate acid of the base NH_3. **If the Brönsted acid is strong, then its conjugate base is weak and vice versa.**

Example 8.1

What will be the conjugate bases for the following Brönsted acids: HF, H_2SO_4 and HCO_3^- ?

Solution

The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are: F^-, HSO_4^- and CO_3^{2-} respectively.

Example 8.2

Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

Solution

The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are: NH_3, NH_4^+ and HCOOH respectively.

Example 8.3

The species: H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base.

Solution

The answer is given in the following table:

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

It may be observed that each conjugate acid has one extra proton and each conjugate base has one proton less.

8.1.3 Lewis Acids and Bases

G.N. Lewis in 1923, defined an acid as an electron pair acceptor and a base as an electron pair donor. As far as bases are concerned, there is not much difference between Brönsted-Lowry and Lewis concepts as a base provides a lone pair in both cases. However, Lewis concept for an acid includes many substances that do not have a

proton. Thus an electron deficient compound like BF_3 that has no proton on it also acts an acid in its reaction with NH_3 by accepting its lone pair. The reaction may be represented by the equation:

$$F_3B + :NH_3 \rightarrow F_3B:NH_3 \quad (8.6)$$

Thus any electron deficient molecule that has no proton may act as Lewis acid. Nearly all metal cations act as Lewis acids, while all ligands (H_2O, NH_3, OH^- etc.) that form complexes with metal ions act as Lewis bases.

Example 8.4

Classify the following species into Lewis acids and Lewis bases and show how these act as such:
(a) HO^- (b) F^- (c) H^+ (d) BCl_3

Solution

(a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair(:OH).
(b) Fluoride ion acts as a Lewis base as it can donate any of its four electron lone pairs.
(c) A proton is a Lewis acid as it can accept a lone pair from bases like hydroxyl ion and fluoride ion.
(d) BCl_3 acts as a Lewis acid as it can accept a lone pair from species like ammonia or amine molecules.

8.2 IONIZATION OF ACIDS AND BASES

Most of the chemical and biological reactions take place in aqueous medium and for this purpose it is useful to discuss the ionization of acids and bases according to their definition by Arrhenius. Like a strong electrolyte (see section 8.1), a strong acid is completely dissociated into hydrogen ion and the corresponding anion. Thus a 0.1 M solution of HCl is fully dissociated to give a solution that is 0.1 M each in hydrogen and chloride ions. Other most commonly encountered strong acids by the chemists are HBr, HI, HNO_3, $HClO_4$, $ClSO_3H$, FSO_3H, $HSbF_6$, and H_2SO_4. In a solution of a strong acid, the main source of hydrogen ion is the acid itself unless the molarity of the solution is equal to or less than 10^{-6} M when the ionization of water has also to be considered (see section 8.2.3). Similarly, a strong base like sodium hydroxide is also completely dissociated in sodium and hydroxyl ions (What is the concentration of hydroxide ion in 0.05 M sodium hydroxide solution?) Other commonly encountered strong bases are LiOH, KOH, RbOH, CsOH, $Ba(OH)_2$ and $Ca(OH)_2$. Most of the acids and bases are weak and are only partially ionized in aqueous solutions. Before we discuss quantitatively the ionization equilibria of the acids and bases, it will be useful to define the pH scale as it is convenient to express the wide range of hydrogen ion concentration in aqueous solutions.

8.2.1 The pH Scale

The pH is defined as the negative logarithm to base 10 of the activity (a_{H^+}) of hydrogen ion. At low concentration the activity of hydrogen ion is numerically equal to its molarity represented by $[H^+]$. The activity of hydrogen ion does not have any units and can be defined by the following equation:

$$a_{H^+} = [H^+]/\text{mol}\,L^{-1}$$

The following equation gives the relation between pH and hydrogen ion concentration:

$$pH = -\log a_{H^+} = -\log \{[H^+]/\text{mol}\,L^{-1}\} \quad (8.7)$$

Thus if a solution is 10^{-3} M in hydrogen ion, its pH = $-\log [10^{-3}] = 3$. In pure and neutral water at 298 K, the concentration of hydrogen ion is 10^{-7} M, hence its pH = $-\log [10^{-7}] = 7$. If an aqueous solution is acidic, its pH is less than 7 and if it is basic its pH is greater than 7. The pH of a solution can be found roughly with the help of pH paper that has different colour in solutions of different pH. Nowadays pH paper is available with four strips on it. The different strips have different colours (Fig.8.2) at the same pH. The pH in the range of 1-14 can be determined with an accuracy of about 0.5 using pH paper. However, pH metres (Fig.8.3) of different size and accuracy are commercially available. These are used routinely in laboratories, factories and fieldwork for the measurement of pH of a variety of fluids up to 0.001 precision. pH metres of the size of a writing pen are now available in the market.

Example 8.5

The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH?

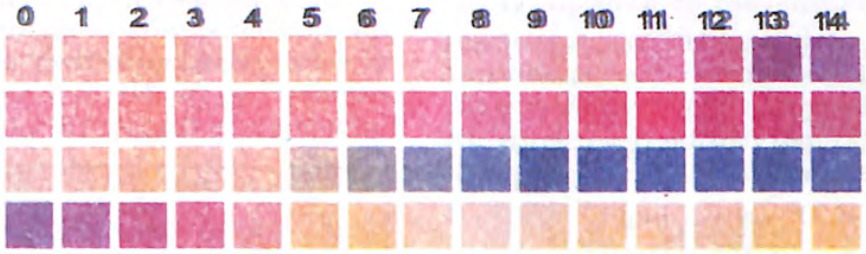


Fig.8.2 *pH-paper with four strips that may have different colours at the same pH*

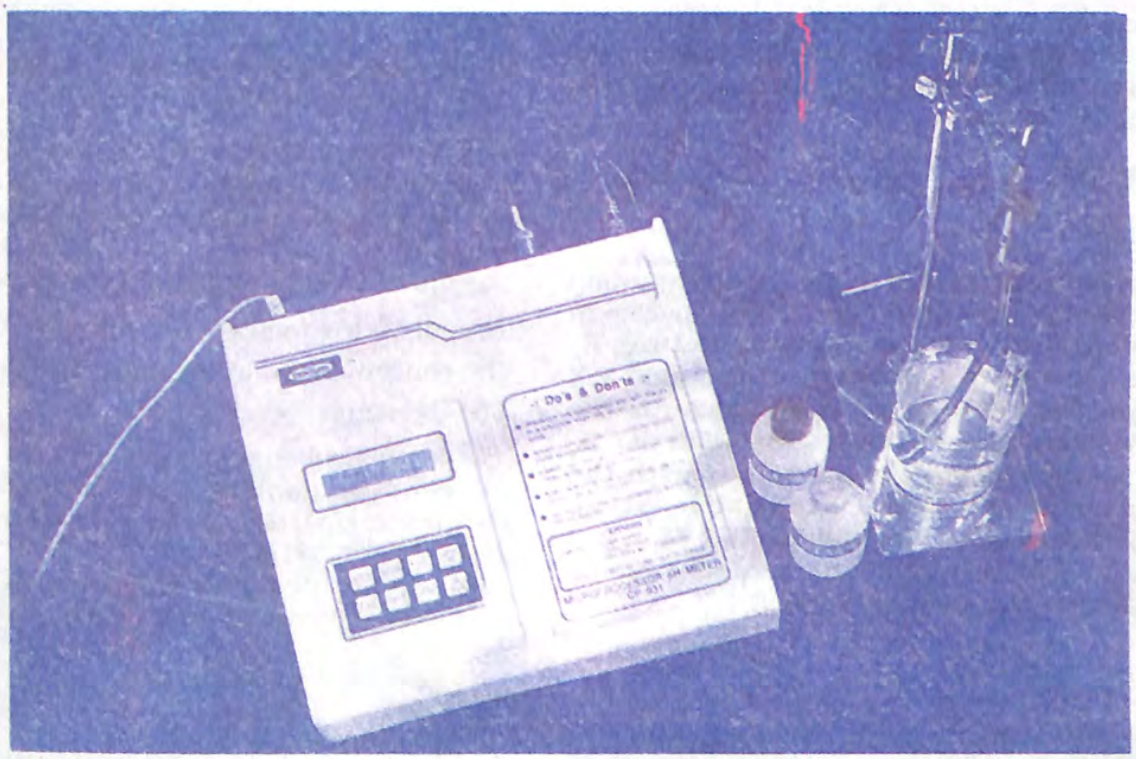


Fig.8.3 *pH metres like shown above are routinely used for accurate measurement of pH of solutions*

Solution

$pH = -\log [3.8 \times 10^{-3}] = - \{ \log [3.8] + \log [10^{-3}] \}$

$= - \{(0.58) + (-3.0)\} = - \{-2.42\} = 2.42$

Therefore, the pH of the soft drink is 2.42 and it can be inferred that it is acidic.

Example 8.6

The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

Solution

$pH = 3.76 = -\log \{[H^+]/\text{mol } L^{-1}\}$,

$\log\{[H^+]/\text{mol } L^{-1}\} = \text{antilog } (-3.76)$

$= \text{antilog } (0.24 - 4.0)$

$[H^+] = \{\text{antilog } (0.24) \times \text{antilog } (-4) \} \text{ mol } L^{-1}$

$= 1.7 \times 10^{-4} \text{ M}$

The pH scale for the hydrogen ion concentration has been so useful that it has been extended to other species and quantities. Thus we have:

$pOH = -\log \{[OH^-]/\text{mol } L^{-1}\}$; $pK_a = -\log (K_a)$ and $pK_b = -\log (K_b)$

Here, K_a is the ionization constant of an acid and K_b is the ionization constant of a base. The ionization constants of acids and bases are defined in the following sections.

8.2.2 Ionization Constant of Weak Acids

Let us consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium between the undissociated species HX and the ions H^+ (aq) and X^- (aq) can be represented by either of the equations:

$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$

($\rightleftharpoons$ Shows reversibility of dissociation)

or simply $HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$ (8.1)

The equilibrium constant for the equation [8.1] called the **dissociation or the ionization constant of the acid,(K_a)** is given by the equation:

$$K_a = \frac{[H^+][X^-]}{[HX]} \quad (8.8)$$

The symbol in bracket in the above equation represents the concentration of that species in terms of molarity. **At a given temperature, K_a is a measure of the strength of the acid HX i.e. larger the value of K_a, the stronger is the acid. As mentioned in Unit 7 we shall use K_a and K_b as dimensionless quantities with the understanding that standard state concentration of all the species is 1 M.**

The values of the ionization constants of some selected acids are given in Table 8.1.

Table 8.1 The Ionization Constants of Some Selected Weak Acids at (298K)

Acid	Ionization Constant, K_a
Hydrofluoric Acid(HF)	3.5×10^{-4}
Nitrous Acid(HNO_2)	4.5×10^{-4}
Formic Acid(HCOOH)	1.8×10^{-4}
Niacin (C_5H_4NCOOH)	1.5×10^{-5}
Acetic Acid (CH_3COOH)	1.74×10^{-5}
Benzoic Acid (C_6H_5COOH)	6.5×10^{-5}
Hypochlorous Acid (HClO)	3.0×10^{-8}
Hydrocyanic Acid (HCN)	4.9×10^{-10}
Phenol (C_6H_5OH)	1.3×10^{-10}

If we know the ionization constant of an acid and its initial concentration then it is possible to calculate the equilibrium concentrations of all the species and also the degree of ionization of the acid and the pH of the solution. **The degree of ionization, α, is defined as the extent up to which the acid is ionized into ions.** We shall illustrate this with the help of a few examples.

It can be seen from Table 8.1 that although all the compounds listed are weak acids, there is great variation in their acid strengths. For example, K_a for HF (3.5×10^{-4}) is about 0.71 million times that for HCN (4.9×10^{-10}).

Example 8.7

The ionization constant of acetic acid is 1.74×10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05M solution. Calculate the concentration of acetate ion in the solution and its pH?

Solution

The problem can be solved in two ways. In the first method, we assume that equilibrium concentrations of various species are as given below:

The initial concentration of the acid = c = 0.05 M

$[H^+(aq)] = [Ac^-(aq)]$ = x an unknown quantity

The concentration of the unionized acid

= [HAc] = 0.05 – x

(Please remember before substitution, we divide concentration terms by Standard Concentration 1 M and multiply activity, by 1 M while mentioning the concentration value.)

Putting these quantities in equation [8.8], we get:

Dissociation constant of the acid,

$$K_a = 1.74 \times 10^{-5} = \frac{(x)(x)}{(c-x)} = x^2/(0.05-x) \quad (8.9)$$

or $x^2 + 1.74 \times 10^{-5}\, x - 8.7 \times 10^{-7} = 0$

The quadratic equation in x can be solved and the two values of the roots are:

$$x = \frac{-1.74 \times 10^{-5} \pm \sqrt{\left\{\left(1.74 \times 10^{-5}\right) + 4 \times 8.7 \times 10^{-7}\right\}}}{2}$$

$= 9.3 \times 10^{-4}$M and -9.3×10^{-4}M (by multiplying by 1 M as indicated above)

The negative root is not acceptable and hence $x = 9.3 \times 10^{-4}$M. This means that the concentration of both hydrogen and acetate ions is equal to 9.3×10^{-4} M and hence the pH of the solution is given by

$pH = -\log[[H^+]/1M] = -\log[0.00093] = 3.03$

The degree of ionization of the acid = α = x/0.05

= 0.00093/0.05 = .0186 or 1.86%.

It can be seen that the quantity 'x' is very small

and can be neglected, compared to 0.05 M in the denominator on the right hand side in the equation [8.9] and it can be simplified to:

$1.74 \times 10^{-5} = x^2/0.05$

or $x = (8.7 \times 10^{-7})^{1/2} = 9.3 \times 10^{-4}$

$[H^+] = 9.3 \times 10^{-4}$M

It can be seen that, with this approximation we get the same value of 'x'. It is always useful to use this approximation when 'c' is large and/ or K_a is small.

In the second method we assume that the degree of dissociation is 'α'. In this case the equilibrium concentration of all the species is given by the equations:

$[H^+] = [Ac^-] = c\,\alpha = 0.05\ \alpha$ M and $[HAc] = c\,(1 - \alpha)$

The equation is quadratic in α but if it is much smaller than 1 it can be neglected in the denominator and we get:

$$\alpha = \sqrt{(K_a/c)} = \sqrt{(1.74 \times 10^{-5} / 0.05)} = 0.0186$$

$$[H^+] = [Ac^-] = c\,\alpha = \sqrt{(cK_a)}$$

$= \sqrt{(0.05 \times 0.0186)} = 0.00093$; or $[H^+] = 0.00093$

pH = -log {(0.00093) = 3.03

Example 8.8

It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a.

Solution

From the pH of the solution, we can calculate the hydrogen ion concentration that is also equal to the concentration of the anion. Thus we have:

$[H^+]/1M = [A^-]/1M = \text{antilog}(-pH) = \text{antilog}(-4.15)$

$= 7.08 \times 10^{-5}$

or $[H^+] = [A^-] = 7.08 \times 10^{-5}$M

The concentration of the undissociated acid

$= (0.01 - 0.000071)$ M $= 0.009929$ M

Therefore, $K_a = (0.000071)^2/(0.009929)$

$= 5.08 \times 10^{-7}$

$pK_a = -\log(K_a) = -\log(5.08 \times 10^{-7}) = 6.29$

Example 8.9

The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

Solution

The concentration of hydrogen ion = $[H^+] = c\,\alpha$

$= 0.1$ M $\times 0.132 = 0.0132$ M

pH $= -\log [H^+]/M = -\log(0.0132) = 1.88$

$K_a = (c\alpha^2)/(1 - \alpha) = (0.1 \times (0.132)^2/ (1 - 0.132)$

$= 2.01 \times 10^{-3}$

$pK_a = -\log(K_a) = -\log(2.01 \times 10^{-3}) = 2.7$

8.2.3 The Ionization Constant of Water and its Ionic Product

It was mentioned earlier that water can also behave as a weak acid and ionize according to the equation:

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

The dissociation constant of water is then given by the equation:

$$K_{a(H2O)} = \{[H^+]\,[OH^-]\}/[H_2O] \qquad (8.10)$$

It has been found that the concentration of hydrogen and hydroxyl ion at 298 K are both equal to 10^{-7} M and the molarity of water in its own pure sample is 1000/18 = 55.55 M. Therefore,

$$K_{a(H2O)} = (10^{-7})^2 / (55.55) = 1.8 \times 10^{-16} \qquad (8.11)$$

As the concentration of water is nearly constant (55.55 M), the product of the concentration of hydrogen and hydroxyl ions, called the *ionic product of water* is given by the equation:

$$K_w = [H_2O]\,K_{a(H2O)} = [H^+]\,[OH^-] \qquad (8.12a)$$

Substituting the value of $K_{a(H2O)}$ and concentration of water in equation (8.12a) at 298 K we obtain:

$$K_w = [H^+]\,[OH^-] = 10^{-14} \qquad (8.12b)$$

Taking negative log of both sides of equation (8.12b), we obtain

$-\log\{[H^+]\,[OH^-]\} = -\log[H^+] - \log[OH^-]$

$$= pH + pOH = 14 \qquad (8.13)$$

This is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is constant.

For example in 0.1 M solution of HCl, the concentration of hydrogen ion is 0.1 M. Therefore, the concentration of hydroxyl ion is given by the equation:

$$\frac{[OH^-]}{M} = \frac{\text{Ionic product of water}}{[a_{H+}]} = \frac{K_w}{[a_{H+}]} = \frac{10^{-14}}{0.1}$$

$[OH^-] = 1 \times 10^{-13}$ M

The pH of neutral water is 7 at 298 K and its solution is acidic when the pH is less than 7 or hydrogen ion concentration is greater than 10^{-7}M and the solution is basic when the hydrogen ion concentration is less than 10^{-7} M or its pH is greater than 7. The pH of some more common substances are given in Table 8.2. It is implied that wherever we use $pK_w = 14$ and pH = 7 for neutral pure water, the temperature is 298K. The variations in pH with temperature are so small that we often ignore them.

Table 8.2 The pH of Some Common Substances

Name of the Fluid	pH	Name of the Fluid	pH
Saturated solution of NaOH	~ 15	Black Coffee	5.0
0.1 M NaOH solution	13	Tomato juice	~4.2
Lime water	10.5	Soft drinks and vinegar	~3.0
Milk of magnesia	10	Lemon juice	~2.2
Egg white, sea water	7.8	Gastric juice	~1.2
Human blood	7.4	1M HCl solution	~0
Milk	6.8	Concentrated HCl	~ -1.0
Human Saliva	6.4		

8.2.4 The Ionization of Bases

The ionization of a base MOH can be represented by the equation:

$$MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq)$$

If the base is weak, it ionizes partially into the cation M^+ and the anion OH^-. If the initial concentration of base is 'c', then the equilibrium concentration of all the species are given by the equations:

$[M^+] = [OH^-] = x$ an unknown quantity and $[MOH] = (c - x)$. These are related to K_b by the equation:

$$K_b = \frac{x^2}{(c-x)} \qquad (8.14a)$$

Where K_b, the equilibrium constant for base ionization is called the *base ionization constant.* Alternatively, if we suppose that the degree of ionization of the base is 'α' then the equilibrium concentrations of all the species are given by: $[M^+] = [OH^-] = c\,\alpha$ and $[MOH] = c\,(1 - \alpha)$ and putting these in equation [8.8] we get

$$K_b = \frac{(c\alpha)^2}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)} \qquad (8.14b)$$

If the value of K_b and the initial concentration, c, are given then it is possible to calculate x and the degree of dissociation of the base by either of the two methods used in calculating the same quantities for the acids. If the values of the degree of dissociation and x are small then the quadratic equations can be simplified as mentioned earlier. The values of the ionization constants of some selected bases, K_b are given in Table 8.3. Ammonia and some amines in water produce hydroxyl ion by the reaction:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Many naturally occurring drugs like codeine, nicotine, quinine and amphetamine are also amines. These are very weak bases and hence their ionization constants are very small.

Table 8.3 The Values of the Ionization Constant of Some Weak Bases at 298 K

Base	K_b
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}
Triethylamine, $(C_2H_5)_3N$	6.45×10^{-5}
Ammonia, NH_3 or NH_4OH	1.77×10^{-5}
Quinine, (A plant product)	1.10×10^{-6}
Pyridine, C_5H_5N	1.77×10^{-9}
Aniline, $C_6H_5NH_2$	4.27×10^{-10}
Urea, $CO(NH_2)_2$	1.3×10^{-14}

Example 8.10

The pH of 0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pK_b.

Solution

From the pH we can calculate the hydrogen ion concentration. Knowing hydrogen ion concentration and the ionic product of water we can calculate the concentration of the hydroxyl ion. Thus we have

$[H^+]$ = antilog (–pH) = antilog (–9.95)
$= 1.12 \times 10^{-10}$ M

$[OH^-]$ = ionic product of water/ $[H^+]$

$= 10^{-14} / (1.12 \times 10^{-10}) = 8.93 \times 10^{-5}$ M

The concentration of the corresponding codenium ion is also the same as that of hydroxyl ion. The concentration of both these ions is very small and hence the concentration of the undissociated base can be taken equal to 0.005 M. Therefore,

$$K_b = \frac{[M^+][OH^-]}{[MOH]} = \frac{(8.93 \times 10^{-5})^2}{0.005} = 1.6 \times 10^{-6}$$

$pK_b = -\log (K_b) = -\log (1.6 \times 10^{-6}) = 5.8$

Example 8.11

What is the pH of 0.001 M aniline solution. The ionization constant of the base can be taken from Table 8.3. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

Solution

The ionization of aniline in water may be represented by the equation:

$C_6H_5NH_2 + H_2O(l) \rightleftharpoons C_6H_5NH_3^+ + OH^-$

We use the equation (8.14a) to calculate

$[OH^-] = x$

$K_b = (x^2)/(c - x)$

The value of the ionization constant is very small, therefore, the quadratic equation can be simplified by neglecting x in comparison to c in the denominator on the right hand side of the equation. Therefore,

$$[OH^-] = x = \sqrt{(c \times K_b)}$$

$$= \sqrt{(0.001 \times 4.27 \times 10^{-10})} = 6.53 \times 10^{-7} M$$

$[H^+] = K_w / [OH^-] = (1 \times 10^{-14}) / (6.53 \times 10^{-7})$

$= 1.53 \times 10^{-8}$ M

pH = $-\log (1.53 \times 10^{-8}) = 7.81$

The degree of ionization,

$$\alpha = \sqrt{\frac{K_b}{c}} = \sqrt{\frac{4.27 \times 10^{-10}}{0.001}}$$

$$= \sqrt{42.7 \times 10^{-8}} = 6.53 \times 10^{-4}$$

It can be seen that the value of x is so small that we are justified to neglect it in comparison with c. In order to find relation between a base and its conjugate acid let us consider the equation:

$B + H_2O \rightleftharpoons BH^+ + OH^-$, (B is a base here)

$K_b = \{[BH^+][OH^-]\} / [B]$

$= \{[BH^+][OH^-][H^+]\} / \{[B][H^+]\}$

$= \{[OH^-][H^+]\}\{[BH^+]/[H^+][B]\}$

$= K_w / K_a$ or $K_a \times K_b = K_w$ (8.15a)

i.e. the product of the ionization constants of the conjugate acids and bases is equal to the ionic product of water. In this case we have

$K_a = K_w / K_b = 1 \times 10^{-14} / (4.27 \times 10^{-10}) = 2.13 \times 10^{-5}$

It may be noted that if we take the negative log of both sides of equation (8.15a), then pK's of the conjugate acid and base are related to each other by the equation:

$pK_a + pK_b = pK_w = 14$ (at 298 K) (8.15b)

8.2.5 Di- and Polybasic Acids and Di- and Polyacidic Bases

Some of the acids like oxalic acid, sulphuric acid and phosphoric acids have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids. The ionization reactions for example for a *dibasic acid* H_2X are represented by the equations:

H_2X (aq) $\rightleftharpoons$ H^+ (aq) + HX^- (aq)

HX^- (aq) $\rightleftharpoons$ H^+ (aq) + X^{2-} (aq)

And the corresponding equilibrium equations are given below:

$Ka_1 = \{[H^+][HX^-]\} / [H_2X]$ and (8.16)

$Ka_2 = \{[H^+][X^{2-}]\} / [HX^-]$ (8.17)

Here Ka_1 and Ka_2 are called the first and second ionization constants respectively of the acid H_2X. Similarly for tribasic acid like H_3PO_4, we have three ionization constants. The values

of the ionization constants for some common polyprotic acids are given in Table 8.4.

Table 8.4 The Ionization Constants of Some Common Polyprotic Acids (298 K)

Acid	Ka_1	Ka_2	Ka_3
Oxalic Acid	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic Acid	7.4×10^{-4}	1.6×10^{-12}	
Sulphurous Acid	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric Acid	Very large	1.2×10^{-2}	
Carbonic Acid	4.3×10^{-7}	5.6×10^{-11}	
Citric Acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Phosphoric Acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

It can be seen that higher order ionization constants (Ka_2 or Ka_3) are smaller than the lower order ionization constants (Ka_1 or Ka_2) of a polyprotic acid.

Similarly polyacidic bases also ionize in steps and we have the corresponding ionization constants like Kb_1, Kb_2 and Kb_3 etc. For example ethylenediamine is a diacidic base and has ionization constants Kb_1 and Kb_2.

8.2.6 Common Ion Effect in the Ionization of Acids and Bases

The products of ionization of an acid are hydrogen ion and the corresponding anion. If any one of the products is added in the acid solution then the acid is ionized to a lesser extent in agreement with Le Chatelier's principle (Unit – 7). Let us consider the example of acetic acid whose dissociation may be represented by its dissociation equilibria

$$HAc\ (aq) \rightleftharpoons H^+\ (aq) + Ac^-\ (aq)$$

$$K_a = \{[H^+]\ [Ac^-]\}/[HAc] \qquad (8.8)$$

If hydrogen ion is provided from any other source, it will combine with the acetate ion and reduce the degree of ionization of acetic acid. Similar will be the effect when anion is added to the equilibrium mixture from external source. Let us illustrate this with the help of a few examples.

Example 8.12

Calculate the degree of ionization of 0.05 M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution is also (a) 0.01 M and (b) 0.1 M in hydrochloric acid?

Solution

The ionization constant of acetic acid = antilog $(-pK_a) = 1.8 \times 10^{-5}$. The value of ionization constant is small and therefore we can obtain the degree of ionization by the approximate relation:

$$\alpha = \sqrt{\{K_a / c\}} = \sqrt{\{1.8 \times 10^{-5} / 0.05\}}$$

$$= 1.9 \times 10^{-2} = 0.019$$

In order to calculate the degree of ionization in presence of hydrochloric acid let us write the equation:

$$K_a = 1.8 \times 10^{-5} = \{[H^+]\ [Ac^-]\}/[HAc]$$

Now the concentration of hydrogen ion arises from two sources i.e. from hydrochloric acid and the ionization of acetic acid.

In case (a) the molarity of HCl is 0.01 M and it is fully dissociated into hydrogen and chloride ions; let the concentration of hydrogen ion be x from the ionization of HAc. This will also be the concentration of acetate ion. Now we have

$[H^+] = 0.01 + x$, and $[Ac^-] = x$ and $[HAc] = (c - x) = (0.05 - x)$

Putting these values in equation (8.8) we have:

$$K_a = \frac{x(0.01 + x)}{(c - x)}$$, as x is very small, we get

$$K_a = \frac{0.01x}{c}$$

or $x = (c\ K_a)/0.01 = (0.05 \times 1.8 \times 10^{-5})/0.01$

$= 9.0 \times 10^{-5}$ M, and the degree of ionization

$= x/c = (9.0 \times 10^{-5})/0.05 = 1.8 \times 10^{-3} = 0.0018$

It can be seen that the degree of ionization decreases almost by a factor of ten. Similarly in case (b):

$x \sim (0.05 \times 1.8 \times 10^{-5})/0.1 = 9 \times 10^{-6}$ M and

$\alpha = x/c = (9 \times 10^{-6})/0.05 = 0.00018$

Once again we find that the degree of ionization has further decreased by a factor of ten.

If instead of hydrochloric acid, if we add sodium acetate the calculations for degree of ionization are performed in the same way and the major source of acetate ion will be sodium acetate.

In a similar way, a base ionizes into cation M^+

and hydroxyl ion (OH^-) and its degree of ionization is affected by the presence of common ions M^+ or OH^-.

Example 8.13

The ionization constant of dimethyl amine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethyl amine is ionized if the solution is also 0.1 M in NaOH.

Solution

The degree of ionization can be calculated from the following equation:

$K_b = 5.4 \times 10^{-4} = \{c\alpha^2\}/(1 - \alpha) = (0.02\ \alpha^2)/(1 - \alpha)$

Solving the quadratic equation we obtain, $\alpha = 0.151$ and from the approximate equation $\alpha \sim \sqrt{(K_b/c)}$, we obtain $\alpha = \sqrt{(5.4 \times 10^{-4}/0.02)} = 0.164$; showing that the approximation is good only to about 8%. When 0.1 M NaOH is present, the source of hydroxyl ion is due to the dissociation of NaOH and that from the ionization of the amine. Thus we have,

$[OH^-] = 0.1 + x$, $[M^+] = x$ and $[MOH] = c - x$

Putting these in the equation for dissociation constant we obtain:

$K_b = 5.4 \times 10^{-4} = \{x\ (0.1 + x)\}/(c - x) \sim (0.1x)/(0.02)$

or $x = 1.08 \times 10^{-4}$ M and the degree of ionization $= (1.08 \times 10^{-4})/0.02 = 0.0054$.

This is much smaller than 0.164, the degree of dissociation obtained in the absence of NaOH.

8.2.7 Hydrolysis of Salts and the pH of Their Solutions

Salt hydrolysis describes the interaction of water and the cation/anion or both of a salt. The pH of the solution gets affected by this interaction. The cations (e.g. Na^+, Rb^+, Ca^{2+}, Ba^{2+} etc.) of the strong bases and anions (e.g. Cl^-, Br^-, I^-, NO_3^- etc.) of strong acids do not hydrolyze and therefore the solutions of salts formed by strong acids and bases are neutral i.e. their pH is 7. On the other hand the solutions of salts formed from strong bases and weak acids are alkaline i.e. their pH is greater than 7. While the solutions of strong acids and weak bases are acidic i.e. their pH is less than 7. We shall now develop quantitative relationship between the pH of the salt solutions, the ionization constants of the acids & bases and the concentration of the salt in the solution.

8.2.8 The Salts of Strong Bases and Weak Acids

Let us consider the solutions of salts like MX formed by a strong base MOH and a weak acid HX. The salt is a strong electrolyte and is completely dissociated into M^+ and X^- ions according to the equation:

$MX\ (s) + H_2O\ (1) \rightarrow M^+(aq) + X^-(aq)$

If the concentration of the salt is 'c' then the concentration of M^+ and X^- is also 'c'. M^+ is the cation of a strong base and therefore it remains as such but the anion X^- reacts with water molecule to give unionized acid. This process is known as hydrolysis and is represented by the equation:

$X^-(aq) + H_2O(1) \rightleftharpoons HX(aq) + OH^-(aq)$

If 'h' is the degree of hydrolysis indicating the extent to which the anion is hydrolyzed and c is the concentration of MX or X^-, and further assuming that the concentration of water remains constant, the equilibrium constant for the reaction called the hydrolysis constant, K_h is given by the equation

$K_h = \{[HX]\ [OH^-]\}/[X^-]$

Multiplying the numerator and the denominator of the right hand side of the above equation by $[H^+]$ we obtain:

$$K_h = \frac{[HX][OH^-][H^+]}{[X^-][H^+]} = K_w/K_a \qquad (8.18)$$

It can be seen that the hydrolysis constant of the salt of weak acid and strong base is related to the ionic product of water and the ionization constant of the weak acid. If 'c' is the concentration of the salt in the solution and 'h' is the degree of hydrolysis, then after the equilibrium is established the concentration of various species in the solutions are given by the equations:

$[X^-] = c\ (1 - h)$ and $[OH^-] = [HX^-] = c\ h$

We then have the quadratic equation:

$$K_h = K_w/K_a = \{(ch)^2\}/\{c(1-h)\} = \frac{ch^2}{(1-h)} \qquad (8.19)$$

The quadratic equation [8.19] can be solved by the usual method but it is simplified if 'h' is small. We have in this case:

$h = \sqrt{\{K_h/c\}} = \sqrt{\{K_w/(K_a c)\}}$ or $[OH^-] = x = c\,h$

$[OH^-] = \sqrt{\{(cK_w)/K_a\}}$

$[H^+] = K_w/[OH^-] = K_w/\sqrt{\{(cK_w/K_a\}} = \sqrt{\{K_w K_a)/c\}}$

$pH = -\log[H^+] = -\log\sqrt{\{(K_w K_a)/c\}}$

$= ½\,[pK_w + pK_a + \log c]$ (8.20a)

At 298 K, the equation becomes:

$pH = 7 + ½\,[pK_a + \log c]$ (8.20b)

We can use equation (8.19) to calculate 'h' and other quantities. If 'h' is small then the equation (8.20b) is used to calculate the pH of the solution. Let us illustrate this with the help of an example.

Example 8.14

Calculate the pH of 0.05 M sodium acetate solution if the pK_a of acetic acid is 4.74.

Solution

K_a = antilog (–4.74) = $10^{-4.74}$ and $K_h = K_w/K_a$

$= 10^{-14}/10^{-4.74} = 10^{-9.26}$

Using equation (8.17) we have:

$10^{-9.26} = 5.55 \times 10^{-10} = ch^2/(1 - h)$

Solving the quadratic equation we obtain

$h = 1.05 \times 10^{-4}$ and $[OH^-] = ch$

$= 0.05 \times 1.05 \times 10^{-4} = 5.25 \times 10^{-6}$ M and

$[H^+] = K_w/[OH^-] = 10^{-14}/(5.25 \times 10^{-6})$

$= 1.905 \times 10^{-9}$ M or pH = –log $[H^+]/M$ = 8.72

In this case the value of 'h' is very small and we can also use the simplified equation (8.20b) to calculate the pH i.e.

pH = 7.0 + ½ (pK_a + log c) = 7.0 + ½ (4.74 + log (0.05)) = 8.72

8.2.9 The Salts of Strong Acids and Weak Bases

The salt MX formed by a strong acid HX and a weak base MOH when dissolved in water dissociates into cation M^+ and anion X^-. The cation undergoes hydrolysis represented by the reaction:

$M^+(aq) + H_2O(l) \rightleftharpoons MOH(aq) + H^+(aq)$

Keeping in view that the concentration of water remains constant in dilute solutions, the equilibrium constant expression for the above reaction may be represented by:

$K_h = \{[MOH][H^+]\}/[M^+]$

Multiplying the numerator and denominator of the right hand side of the above equation by $[OH^-]$ we obtain

$K_h = \{MOH][H^+][OH^-]\}/\{[M^+][OH^-]\} = K_w/K_b$ (8.21)

It can be seen that hydrolysis constant of the salt of a strong acid and a weak base is related to the ionic product of water and the ionization constant of the base. If 'c' is the concentration of the salt in the solution, 'h' is its degree of hydrolysis then equilibrium concentrations of various species are given by the equations:

$[MOH] = [H^+] = ch$ and $[M^+] = c(1 - h)$

Putting these in the equilibrium equation we have:

$K_h = K_w/K_b = \{(ch)^2\}/\{c(1 - h)\} = (c\,h^2)/(1 - h)$ (8.22)

The quadratic equation [8.22] in 'h' can be solved by the usual method but it can be simplified considerably if 'h' is small. In this case we have:

$h = (K_h/c)^{1/2} = \{K_w/(K_b c)\}^{1/2}$ and $[H^+] = c\,h$

$= \{(K_w c)/K_b\}^{1/2}$

Taking negative log of the hydrogen ion concentration in the above equation we obtain

$-\log[H^+] = -\log\{K_w\,c)/K_b\}^{1/2} = ½\,(pK_w - \log c - pK_b)$ or

$pH = ½\,(pK_w - \log(c) - pK_b)$ (8.23a)

At 298 K, the equation becomes:

$pH = 7 - ½\,(\log c + pK_b)$ (8.23b)

We shall illustrate the use of the above equations for calculating the degree of hydrolysis and the pH of a solution of a salt of strong acid and a weak base.

Example 8.15

The ionization constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Calculate the hydrolysis constant of ammonium chloride and pH of 0.04 M ammonium chloride solution.

Solution

Ammonium choride is the salt of a strong acid and weak base and hence its hydrolysis constant is equal to:

$K_h = K_w/K_b = 1 \times 10^{-14}/(1.77 \times 10^{-5}) = 5.65 \times 10^{-10}$

The degree of hydrolysis 'h' can be calculated using the equation:

$K_h = (ch^2)/(1 - h) = (0.04\ h^2)/(1 - h) = 5.65 \times 10^{-10}$ or $h = 1.19 \times 10^{-4}$ and

$[H^+] = c \times 1.19 \times 10^{-4} = 0.04 \times 1.19 \times 10^{-4}$ M

$= 4.76 \times 10^{-6}$ M or pH = 5.32

It can be seen that 'h' is very small and we can use the simplified equations to calculate the degree of hydrolysis and the pH of the solution.:

$h = (K_h/c)^{1/2} = (5.65 \times 10^{-10}/0.04)^{1/2} = 1.19 \times 10^{-4}$

and $pH = 7.0 - \frac{1}{2}(\log c + pK_b)$

$= 7 - \frac{1}{2}\{\log (0.04) - \log (1.77 \times 10^{-5})\}$

$= 7 - \frac{1}{2}(-1.40 + 4.76) = 5.32$

It can be seen that the pH is less than 7 and as mentioned earlier the solution of a salt of weak base and strong acid is acidic.

8.2.10 The Salts of Weak Bases and Weak Acids

Now we shall try to calculate the hydrolysis constant of a salt MX formed by the weak base MOH and the weak acid HX. The salt in aqueous solution is completely dissociated into the ions and both of these now hydrolyze in water by the reaction:

$M^+(aq) + X^-(aq) + H_2O(l) \rightleftharpoons MOH(aq) + HX(aq)$

Assuming that in dilute solution the concentration of water remains constant, the hydrolysis constant is given by the equation:

$K_h = \{[MOH][HX]\}/\{[M^+][X^-]\}$

Multiplying the right hand side both in the numerator and the denominator by $[H^+][OH^-]$ we obtain:

$K_h = \{[MOH]/[M^+][OH^-]\} \cdot \{[HX]/([H^+][X^-])\} \times \{[H^+][OH^-]\} = K_w/(K_b \times K_a)$ (8.24)

It can be seen that the hydrolysis constant of the salt of a weak acid and a weak base is related to ionic product of water and the ionization constants of the acid and base from which it is formed. If 'c' is the concentration of the salt and 'h' its degree of hydrolysis, then at equilibrium, the concentrations of various species are given by the relations:

$[MOH] = [HX] = c\ h$ and $[M^+] = [X^-] = c\ (1 - h)$

and we have now:

$K_h = (ch)^2/\{(c\ (1 - h)\}^2 = \{h/(1 - h)\}^2$ or

$h/(1 - h) = (K_h)^{1/2}$ (8.25)

It can be seen that the degree of hydrolysis is independent of the concentration of the salt and is related to the square root of the hydrolysis constant by the equation:

$h = K_h^{1/2}/(1 + K_h^{1/2})$ (8.26)

The concentration of the hydrogen ion can be calculated using the equation for the ionization constant of the acid, HX:

$K_a = [H^+][X^-]/[HX]$

or $[H^+] = K_a\ [HX]/[X^-] = K_a\ \{(ch)/(c(1 - h)\}$

$= K_a\ (h/(1 - h))$ or

$pH = -\log [H^+] = -\log K_a - \log(h) + \log(1-h)$ (8.27a)

$= pK_a - \log(h) + \log(1-h)$

If K_h is small then 'h' is also small and we have $h \sim K_h^{1/2}$ and $(1 - h) \sim 1$ and we have

$pH = pK_a - \log (h) = pK_a - \{\log (K_h)^{1/2}\}$

$= \frac{1}{2}\{pK_w + pK_a - pK_b\}$ (8.27b)

and at 298 K we have:

$pH = 7 + \frac{1}{2}(pK_a - pK_b)$ (8.27c)

It can be seen from equation (8.25c) that the pH of the solution depends on the difference of pK_a and pK_b. If it is positive then the pH of the solution is > 7 and if it is negative then the pH is < 7.

Example 8.16

The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the hydrolysis constant of ammonium acetate at 298 K and also the degree of hydrolysis and pH of its (a) 0.01 M and (b) 0.04 M solutions.

Solution

From the pKs of the acid and base, we can calculate their ionization constants. Thus we have:

$K_a = \text{antilog}(-pK_a) = 10^{-4.76} = 1.74 \times 10^{-5}$ and

$K_b = \text{antilog}(-pK_b) = 10^{-4.75} = 1.77 \times 10^{-5}$ and

$K_h = K_w/(K_a K_b)$ or at 298 K.

$K_h = 10^{-14}/(1.74 \times 10^{-5} \times 1.77 \times 10^{-5}) = 3.25 \times 10^{-5}$

It can be seen that K_h is small and, therefore,

$h = (K_h)^{1/2} = (3.25 \times 10^{-5})^{1/2} = 5.7 \times 10^{-3}$

and using equation (8.27c) we have,

pH = 7 – ½ (4.76 – 4.75) = 7.005

It has already been shown that the degree of hydrolysis and the pH are independent of concentration and therefore we have the same answer (i.e. 7.005) for parts (a) and (b) of the question.

Example 8.17

Calculate the degree of hydrolysis and the pH of 0.02 M ammonium cyanide solution at 298 K. The necessary data may be taken from the Tables 8.1 and 8.3.

Solution

The hydrolysis constant, $K_h = K_w (K_a K_b)$; now putting the values from tables we obtain

$K_h = 10^{-14}/(4.99 \times 10^{-10} \times 1.77 \times 10^{-5}) = 1.132$ and $K_h^{1/2} = 1.06$

It can be seen that hydrolysis constant is not small and for calculating 'h' we use the equation:

$h = K_h^{1/2}/(1 + K_h^{1/2}) = 1.06/2.06 = 0.51$ and

$pH = pK_a - \log(h) + \log(1 - h)$
$= -\log(4.99 \times 10^{-10}) - \log(0.51) + \log(1 - 0.51)$
$= 9.30$

8.3 THE ACID-BASE TIRATIONS USING INDICATORS

The reaction between an acid and base is called *neutralization*. It is very fast and the equilibrium constant for a neutralization reaction is so large that it nearly proceeds to completion. An acid-base titration is a simple and convenient volumetric method for quantitatively estimating the concentration of one if that of the other is known. A known volume of the solution of an acid or base is transferred to a titration flask with the help of a pipette (available in various sizes from 0.01 mL to 50.0 mL). We add an indicator like litmus solution to the titration flask and start adding known volumes of the other solution in steps with the help of a burette. The end point of the titration is noted by the change in the colour of the indicator. For accurate estimation it is necessary for it to coincide with the equivalence point corresponding to the stoichiometric amounts of the acid and base in the neutralization reaction. We already know that litmus solution is red in the acidic region and blue in the basic region. A number of weak organic acids can act as indicators if the unionized acid HIn and its anion have different colours.

The colour of the indicator is in between that of the corresponding acid and its anion. Methyl organge has red colour in the acidic region and yellow colour in the alkaline region. The choice of indicator depends on the abrupt change of the pH during neutralization process near the equivalence point. The colours of some of the common indicators in the acidic and basic regions are given in Table 8.5.

In the following sections we shall study neutralization between acids and bases of different strengths and the choice of suitable indicator for these titrations.

8.3.1 The Titration of a Strong Acid with a Strong Base

We already know that HCl is a strong acid and NaOH is a strong base. We now consider titration between their 0.1 M solutions. Let us take 50 mL of 0.1 M HCl solution with the help of a pipette in a titration flask. We know the pH of the solution is 1 and there are $(0.1 \times 50)/1000 = 50 \times 10^{-4}$ mol of HCl in 50 mL of the solution. Noting that the strong acid and base are completely dissociated in aqueous solutions, the neutralization reaction is represented by the equation:

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Cl^-(aq) + Na^+(aq) + H_2O(l)$$

Table 8.5 Colours of Some Common Indicators in Different pH range

	Colour in acidic and basic regions	pH	pH	
Methyl Orange	Red	<3.1	>4.5	yellow
Bromocresol Green	Yellow	<3.8	>4.6	blue
Methyl Red	Pink	<4.2	>6.2	yellow
Bromocresol Purple	Yellow	<5	>6.8	purple
Bromothymol Blue	Orange	<6.0	>7.5	blue
Phenophthalein	Colourless	<8.3	>10	pink
Thymolphthalein	Colourless	<9.3	>10.5	blue

According to the stoichiometry of the reaction one mole of acid requires one mole of base for neutralization. It can be seen that Cl^- and Na^+ do not react and the actual neutralization reaction between a strong acid and base is represented by the equation:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(1)$$

This is further supported by the fact that the enthalpy of the neutralization between all strong acids and bases is nearly same (-57.1 kJ/mol) and the reaction is represented by the above equation. Now let us see how the number of moles of HCl in the solution taken in the titration flask and its pH change as NaOH solution is added to it. If we add v mL of 0.1 M NaOH it will neutralize v mL of 0.1 M HCl leaving behind (50 – v) mL of 0.1 M HCl diluted to (50 + v) mL. Therefore, molarity of acid in the mixture at any stage up to 50 mL of addition of NaOH is given by the equation

$$\text{Molarity of HCl} = \left(\frac{50 - v}{50 + v}\right) 0.1 \text{ M} = [H^+]$$

Therefore, we can determine the pH of the solution from the known concentration of hydrogen ion. The calculated values of pH are given in Table 8.6. After 50 mL of 0.1 M NaOH solution is added, the acid is completely neutralized and its pH is 7.0. Further addition of the solution of NaOH will give a solution (v-50) 0.1 M NaOH diluted to (50 + v) mL and the concentration of NaOH and hence of hydroxyl ion are given by

$$[\text{NaOH}] = [OH^-] = \frac{(v - 50)0.1}{(50 + v)} \text{ M}$$

Knowing the concentration of the hydroxyl ion, we can calculate the hydrogen ion concentration and hence the pH.

The calculated values of pH against volume of sodium hydroxide solution added are plotted in Fig.8.4. The plot is called pH titration curve and has many interesting features. It can be seen that up to the addition of 49.9 mL of base solution, the pH of the solution changes slowly i.e. only from 1 to 4.

After 49.9 mL, just addition of another 0.1 ml base solution the pH changes from 4 to 7 and the solution is now a 0.05 M solution of the salt (NaCl) of the acid and the base. It can be seen that just by further addition of 0.05 mL of NaOH solution pH jumps from 7 to 9.7.

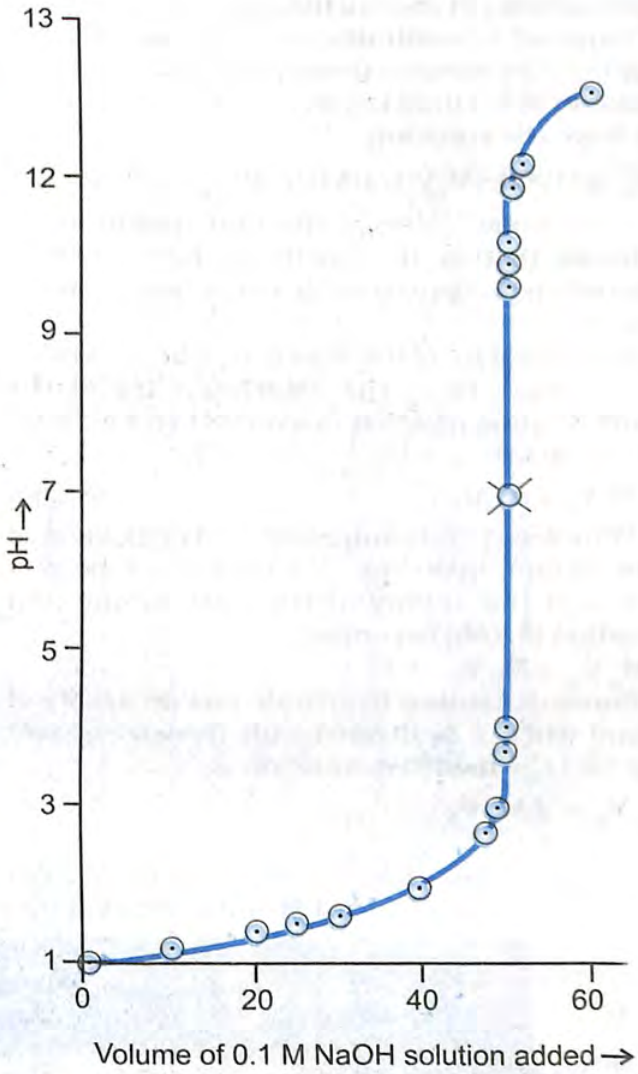


Fig.8.4 *The pH titration curve for titration of 50 mL of 0.1 M HCl solution against 0.1 M NaOH solution. Note the inflection in pH near the equivalence point*

There is an inflection point in the pH of the solution and a number of indicators change their colours over this large change in pH and therefore all of these can be used to note the end point. Thus several indicators like methyl orange, methyl red and phenolphthalein can be used to determine the end point that coincides with the equivalence point. Moreover we can take either of the acid or base as the titrate (the solution that is to be titrated) or as titrant (solution with which titration is performed) using the same indicator. We can determine the volume V_b of the base of molarity M_b required to neutralize volume, V_a of the acid of molarity M_a from the end point. According to the

stoichiometry of the reaction one mole of the base is required to neutralize one mole of the acid. The number of moles present in V mL solution of molarity M is equal to (MV)/1000 and therefore we have the equation:

$(M_a V_a)/1000=(M_b V_b)/1000$ or $M_a V_a = M_b V_b$ (8.28a)

If we know three of the four quantities in equation (8.28a), the fourth can be calculated. The technique is reasonably simple and accurate upto 0.1%.

If the basicity of the acid is n_a and the acidity of the base is n_b the stoichiometry of the neutralization reaction is modified and we have the equation:

$$n_a M_a V_a = n_b M_b V_b \qquad (8.28b)$$

Thus if we titrate sulphuric acid or oxalic acid with sodium hydroxide, the basicity of the acid is 2 and the acidity of the base is one and equation (8.28b) becomes:

$$2 M_a V_a = M_b V_b$$

Similarly barium hydroxide has an acidity of 2 and when it is titrated with monobasic acid like HCl the modified equation is

$$M_a V_a = 2 M_b V_b$$

8.3.2 Titration of Weak Acids and Weak Bases

The pH titration curve of a weak acid (acetic acid) against a strong base (sodium hydroxide) is shown in Fig.8.5. The pH at various stages of addition of alkali can be calculated from the known concentration of the acetic acid and sodium acetate as shown in section 8.2.6. It can be seen that there is an inflection point near the equivalence point only from 7.46 to 10.00 and we can use only phenolphthalein as a suitable indicator.

Similarly the pH titration curve of a weak base against a strong acid is shown in Fig.8.6. Once again the change in pH at the equivalence point is from 6.55 to 4.00. Here only methyl red can be used as an indicator. It may be mentioned here that there is no suitable indicator for the titration of a weak acid against a weak base.

If we plot pH against the volume of HCl solution (Fig.8.6), we get the pH titration curve in which as expected the pH of the solution decreases. Initially the pH decreases very fast as free hydroxyl ion is consumed. After which due to the presence of common ammonium ion the ionization of ammonium hydroxide decreases

Table 8.6 The Values of Various Quantities during the Titration of 50 mL of 0.1 M HCl solution against 0.1 M NaOH solution

v(NaOH) added/mL	$[HCl] = [H^+] = \left(\frac{50 - v}{50 + v}\right) 0.1M$	$[NaOH]=[OH^-]=\left(\frac{v - 50}{50 + v}\right) 0.1M$	$[H^+]$ in the Solution	pH of the Solution
0.0 mL	0.1000		0.1 M	1.00
10.0	0.0667		0.0667	1.18
20.0	0.0429		0.0429	1.39
25.0	0.0333		0.0333	1.48
30.0	0.0250		0.0250	1.60
40.0	0.0111		0.0111	1.96
48.0	0.0022		0.0022	2.69
49.0	0.0010		0.0010	3.00
49.8	0.0002		0.0002	3.70
49.9	0.0001		0.0001	4.00
50.0		0.05M NaCl	10^{-7}	7.00
50.05		0.5×10^{-4} (NaOH)	2×10^{-10}	9.70
50.1		1×10^{-4}	10^{-10}	10.00
50.2		2×10^{-4}	5×10^{-11}	10.30
51.0		1×10^{-3}	1×10^{-11}	11.0
52.0		2×10^{-3}	5×10^{-12}	11.3

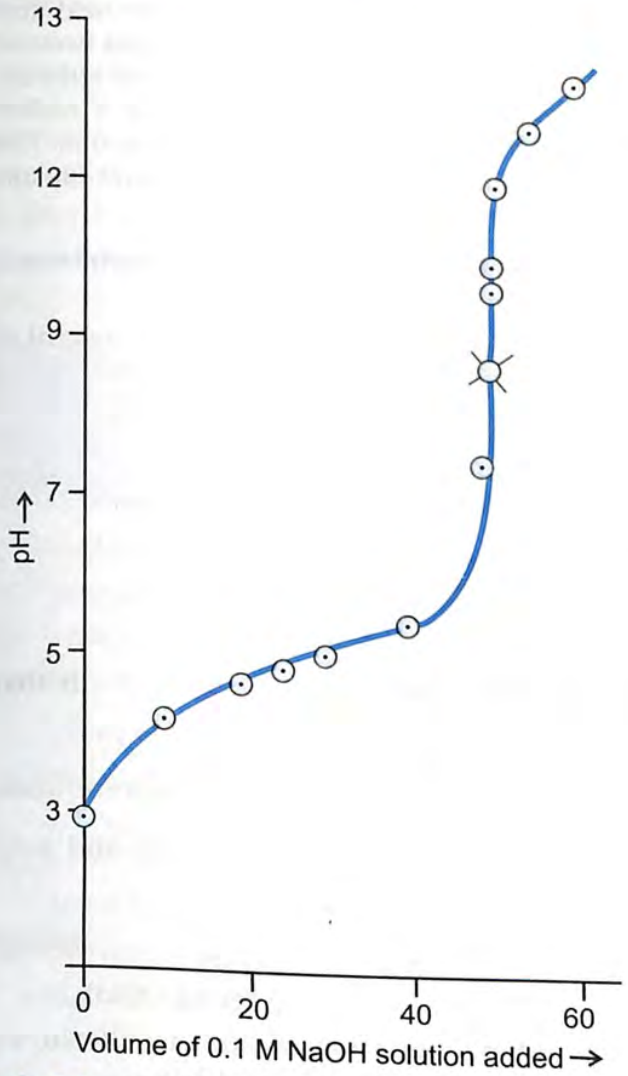


Fig.8.5 *pH titration curve of 50 mL of a 0.1 M acetic acid against 0.1 M NaOH solution*

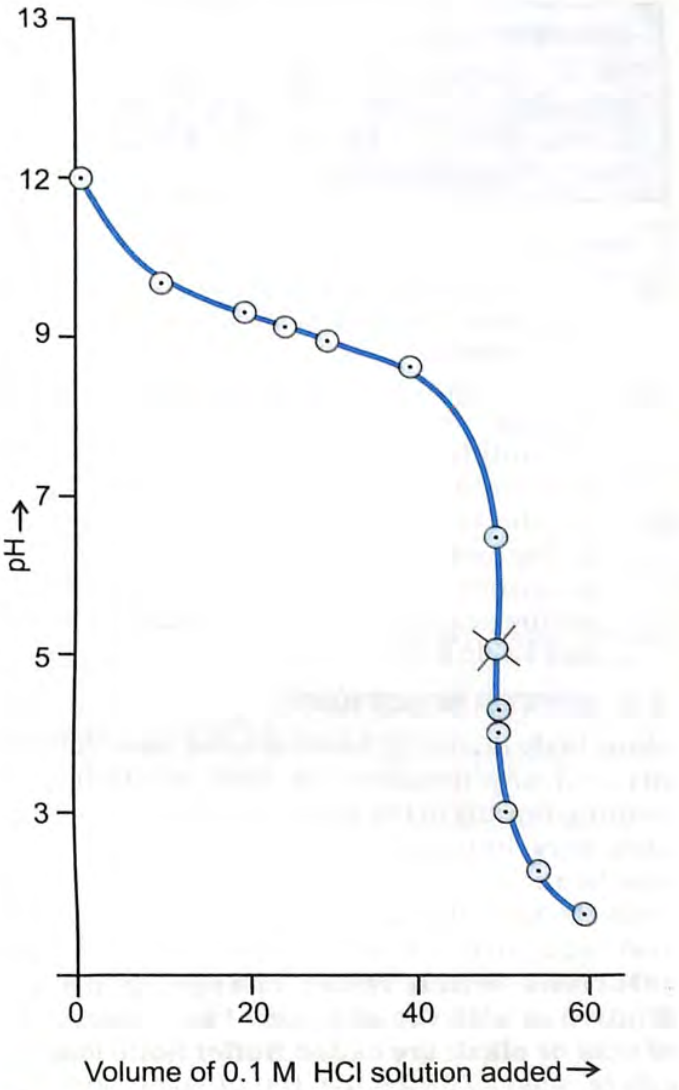


Fig.8.6 *pH titration curve of 50 mL of a 0.1 M NH_4OH against 0.1 M HCl solution*

and at 50% neutralization pH =pK_w - pK_b = 9.25. At the equivalence point, there is an inflection point and pH decreases to 4.30 after 50.05 mL of acid solution is added. It can be seen that it will be quite appropriate to use methyl orange or methyl red as indicator. It may be noted that phenolphthalein is not a suitable indicator in this titration as the end point and equivalence point do not coincide. The titration of a very weak base with strong acid can not be performed due to hydrolysis of its salt as no suitable indicator will give the end point coinciding with the equivalence point. In the same way we do not have suitable indicator for the titration of a weak acid against a weak base or vice versa.

Example 8.18

A solution gives the following colours with different indicators: Methyl orange – yellow; methyl red – yellow, and bromothymol blue – orange. What is the pH of the solution?

Solution

The colour in methyl orange indicates that pH > 4.5; colour in methyl red indicates that pH > 6.0; and colour in bromothymol blue indicates that pH < 6.3. Therefore the pH of the solution is between 6.0 to 6.3.

Example 8.19

What indicators will be suitable for the following acid base titrations: (a) HCOOH against NaOH (b) HBr against KOH and (c) NH_4OH against HNO_3.

Solution

(a) For the titration of a weak acid and a strong base phenolphthalein and thymolphthalein are suitable.

(b) For the titration of a strong acid against a strong base bromothymol blue, phenolphthalein, methyl orange and thymolphthalein are suitable and,

(c) For the titration of a weak base against a strong acid methyl orange, bromocresol green and methyl red are suitable. You can get the answer by looking at Figs.8.4 to 8.6 and Table 8.5.

8.4 BUFFER SOLUTIONS

Many body fluids e.g. blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body. The control of pH is also very important in many chemical and biochemical processes. Many medical and cosmetic formulations require that these be kept and administered at a particular pH. **The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.** It can be seen in Figs.8.4–8.6 that some portions of the titration curves are flat i.e. the pH of titration mixtures change very little even on addition of acid or base. It can be seen that these portions are generally mixtures of acid and salt or base and salt. A solution of a strong acid (e.g. HCl) of reasonable concentration (~ 0.1 M) acts as a buffer (see Fig.8.4). The acid is completely dissociated and all the hydrogen ions are present in the free form. Initial pH increases only by 0.3 even after half of the acid is neutralized i.e. its concentration is reduced to less than 0.05. Same is true for a strong base whose solution act as a buffer at higher pH (see later parts of the titration curves in Figs.8.4 and 8.5) which now corresopond to dilute solutions of NaOH in presence of some salt. We will now show that a buffer solution of known pH can be prepared from the knowledge of pK_a of the acid or pK_b of base and by controlling the ratio of the salt and acid or salt and base. A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide acts as a buffer around 9.25. We shall now discuss the preparation of some buffer solutions and explain their buffer action.

8.4.1 Buffer Solution of Sodium Acetate and Acetic Acid

We already know that the ionization constant of an acid is given in equation:

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

Taking logarithm on both sides we get

$$pK_a = pH - \log \frac{[X^-]}{[HX]}$$

$$\text{or} \quad pH = pK_a + \log \frac{[X^-]}{[HX]} \qquad (8.29a)$$

The quantity $\frac{[X^-]}{[HX]}$ is the ratio of concentration of salt (or conjugate base of acid) and acid present in this mixture.

$$\text{Therefore, } pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \qquad (8.29b)$$

$$= 4.76 + \log \{[\text{Salt}]/[\text{Acid}]\}$$

The above equation (8.29b) is known as Henderson – Hasselbalch equation.

Let us consider, 100 mL of a buffer solution that is 0.05 M, each in acetic acid and sodium acetate. If we substitute their concentrations in the above equation we obtain:

$pH = 4.76 + \log (0.05/0.05) = 4.76$

Now the solution has 50×10^{-4} ([0.05×100]/1000) mol of acetic acid and sodium acetate each. The addition of 1 mL of 0.1 NaOH solution means addition of 1×10^{-4} mol of NaOH, which neutralizes 1×10^{-4} mol of acetic acid and produces 1×10^{-4} mol of sodium acetate. Now we have:

$[NaAc] = \{(50 + 1) \times 10^{-4})\}\ 1000/V$ M and

$[HAc] = \{(50 - 1) \times 10^{-4})\}\ 1000/V$ M

Here V is the total volume of the solution after addition of acid or base and when we take the ratio of their concentrations, the factor ($10^{-4} \times 1000$)/V cancels out and we obtain:

$pH = 4.76 + \log (51/49) = 4.76 + 0.02 = 4.78$

We note that addition of 1 mL of 0.1 M NaOH does not change the pH of the solution appreciably and we have a good buffer solution. Similarly if we add 1 mL of 0.1 M HCl solution, it converts 1×10^{-4} mol of sodium acetate into acetic acid and we have:

[NaAc] $= \{(50 - 1) \times 10^{-4}\}\ 1000/V$ M and

[HAc] $= \{(50 + 1) \times 10^{-4}\}\ 1000/V$ M and we obtain

pH $= 4.76 + \log (49/51) = 4.76 - 0.02 = 4.74$

Example 8.20

How much volume of 0.1 M HAc should be added to 50 mL of 0.2 M NaAc solution if we want to prepare a buffer solution of pH 4.91.

Solution

Now using the equation:

$pH = pK_a + \log ([salt]/[acid]$

or $4.91 = 4.76 + \log ([salt]/[acid])$

$$\frac{\text{number of moles of salt}}{\text{number of moles of acids}} = \frac{[NaAc]}{[HAc]}$$

$= \text{antilog}\ (4.91 - 4.76) = 1.41$

Number of moles of NaAc in the given solution

$= (0.2 \times 50)/1000$

Number of moles of acid required

$= (0.1 \times V)/1000$

Therefore $V = (0.2 \times 50)/(1.41 \times 0.1) = 70.92$ mL

Volume of 0.1 M acetic acid required is 70.92 mL.

Example 8.21

The ionization constant of formic acid is 1.8×10^{-4}. Around what pH will its mixture with sodium formate give buffer solution of higher capacity. Calculate the ratio of sodium formate and formic acid in a buffer of pH 4.25.

Solution

Buffer capacity is defined as the rate of change in pH with number of moles of acid or base added. Thus we have

Buffer capacity $= dpH/dn_{\text{acid or base}}$

It has been found that buffer capacity is maximum near the pK_a of the acid (provided total numbers of moles of salt and acid remain constant). In this case

$pK_a = -\log (1.8 \times 10^{-4}) = 3.74$. This is the pH of high capacity buffer. In order to obtain a buffer solution of pH 4.25 we have

$\log [salt]/[acid] = pH - pK_a = 4.25 - 3.74$ or

$[salt]/[acid] = \text{antilog}\ (0.51) = 3.24$

8.4.2 Alkaline Buffer Solution($NH_4Cl + NH_4OH$)

We can treat a mixture of ammonium chloride and ammonium hydroxide in two ways. We can consider either the reaction:

$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

or we take the conjugate acid NH_4^+ and consider the reaction:

$NH_4^+(aq) + H_2O(1) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

or $NH_4^+(aq) + H_2O(1) \rightleftharpoons NH_3(aq) + H^+(aq)$

To calculate the pH, we arrange this equation in the form

$$[H^+(aq)] = K_a \frac{[NH_4^+]}{[NH_3]}$$

Taking negative logarithm on both side, we get

$$pH = pK_a - \log \frac{[NH_4^+]}{[NH_3]}$$

It may be noted that $pK_a + pK_b = 14$ and pK_a for $NH_4^+ = 9.25$.

Therefore, $$pH = 9.25 - \log \frac{[NH_4^+]}{[NH_3]}$$

or $$pH = 9.25 + \log \frac{[NH_3]}{[NH_4^+]}$$

or $$pH = 9.25 + \log \frac{[\text{Base}]}{[\text{Conjugate acid}]}$$

It is to be noted that the highest buffer capacity should be around 9.25 and furthermore concentration of ammonia is actually the concentration of ammonium hydroxide.

Example 8.22

How much of 0.3 M ammonium hydroxide should be mixed with 30 mL of 0.2 M solution of ammonium chloride to give buffer solutions of pH 8.65 and 10.

Solution

pH =9.25+log{[NH_4OH]/[NH_4^+]} or

[NH_4OH]/[NH_4^+]=antilog (pH – pK_a)

but [NH_4^+] = [NH_4Cl] and we have

for pH 8.65, [NH_4OH]/[NH_4Cl] = antilog (8.65 – 9.25) = antilog (-0.60) = 0.25 or

[NH_4OH]/[NH_4Cl] = {0.3 × V/1000}/{0.2×30/1000} = 0.25 and we have = 5.02 mL and similarly for pH 10 we have

{0.3 ×V/1000}/{0.2×30/1000} = antilog (10-9.25) and we have V = 12.94 mL.

8.5 SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

We have already known that the solubility of ionic solids in water varies a great deal. Some of these are so soluble that they are hygroscopic in nature and even absorb water vapours from atmosphere. Others have so little solubility that in common parlance these are called insoluble. The solubility depends on a number of factors important among which are the lattice energy of the salt and how well the ions are hydrated in the aqueous solution. Each salt has its characteristic solubility and its dependence on temperature. We classify salts on the basis of their solubility in the following three categories

Category I	Soluble	Solubility > 0.1 M
Category II	Slightly soluble	0.01<Solubility < 0.1 M
Category III	Sparingly soluble	Solubility < 0.01 M

We shall now consider the equilibrium between the sparingly soluble ionic salt and its saturated aqueous solution.

8.5.1 Solubility Product Constant

Let us now have a solid salt like barium sulphate in contact with its saturated aqueous solution. If the dissolution process is represented by the equation:

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$, then equilibrium constant is given by the equation:

$K = \{[Ba^{2+}][SO_4^{2-}]\}/[BaSO_4]$

For a pure solid substance the concentration remains constant and we can write

$$K_{sp} = K[BaSO_4] = [Ba^{2+}][SO_4^{2-}] \quad [8.30]$$

We call K_{sp} the *solubility product constant or simply solubility product*. The experimental value of K_{sp} in equation [8.30] at 298K is 1.1×10^{-10}. This means that for solid barium sulphate in equilibrium with its saturated solution, the product of the concentrations of barium and sulphate ions is equal to its solubility product constant. The concentrations of the two ions will be equal to the molar solubility of the barium sulphate. If molar solubility is S, then $1.1 \times 10^{-10} = (S)\,(S) = S^2$ or $S = 1.05 \times 10^{-5}$.

Thus, molar solubility of barium sulphate will be equal to 1.05×10^{-5} mol L^{-1}.

A salt may give on dissociation two or more than two anions and cations carrying different charges. For example, if we consider a salt like *zirconium phosphate* its molecular formula is $(Zr^{4+})_3\,(PO_4^{3-})_4$ and it dissociate into 3 zirconium cations of charge +4 and 4 phosphate anions of charge –3. If the molar solubility of zirconium phosphate is S, then it can be seen from the stoichiometry of the compound that

$[Zr^{4+}] = 3S$ and $[PO_4^{3-}] = 4S$ and $K_{sp} = (3S)^3\,.(4S)^4 = 3^3 \times 4^4\,(S)^7 = 6912\,(S)^7$

or $S = \{K_{sp}/(3^3 \times 4^4)\}^{1/7} = (K_{sp}/6912)^{1/7}$

A solid salt of the general formula $M_x^{z+}X_y^{z-}$ with molar solubility S in equilibrium with its saturated solution may be represented by the equation:

$M_xX_y(s) \rightleftharpoons xM^{z+}(aq) + yX^{z-}(aq)$

And its solubility product constant is given by:

$$K_{sp} = [M^{z+}]^x\,[X^{z-}]^y = (xS)^x\,(yS)^y = x^x\,.\,y^y\,.\,S^{(x+y)} \quad (8.31)$$

$$S^{(x+y)} = \frac{K_{sp}}{x^x\,.\,y^y}$$

$$S = \left(\frac{K_{sp}}{x^x\,.\,y^y}\right)^{\frac{1}{x+y}} \quad (8.32)$$

The term K_{sp} in equation (8.31) is given the symbol Q_{sp} (see unit 7) when the concentrations of one or more species are not the concentrations under equilibrium. Obviously under equilibrium conditions $K_{sp} = Q_{sp}$ but otherwise it gives the direction of the processes of precipitation or dissolution. The solubility product constants of a number of common salts at 298 K are given in Table 8.7.

Table 8.7 The Solubility Product Constants, K_{sp} of Some Common Ionic Salts at 298 K.

Name of the Salt	Formula	K_{sp}
Silver Bromide	AgBr	5.0×10^{-13}
Silver Carbonate	Ag_2CO_3	8.1×10^{-12}
Silver Chromate	Ag_2CrO_4	1.1×10^{-12}
Silver Chloride	AgCl	1.8×10^{-10}
Silver Iodide	AgI	8.3×10^{-17}
Silver Sulphate	Ag_2SO_4	1.4×10^{-5}
Aluminium Hydroxide	$Al(OH)_3$	1.3×10^{-33}
Barium Chromate	$BaCrO_4$	1.2×10^{-10}
Barium Fluoride	BaF_2	1.0×10^{-6}
Barium Sulphate	$BaSO_4$	1.1×10^{-10}
Calcium Carbonate	$CaCO_3$	2.8×10^{-9}
Calcium Fluoride	CaF_2	5.3×10^{-9}
Calcium Hydroxide	$Ca(OH)_2$	5.5×10^{-6}
Calcium Oxalate	CaC_2O_4	4.0×10^{-9}
Calcium Sulphate	$CaSO_4$	9.1×10^{-6}
Cadmium Hydroxide	$Cd(OH)_2$	2.5×10^{-14}
Cadmium Sulphide	CdS	8.0×10^{-27}
Chromic Hydroxide	$Cr(OH)_3$	6.3×10^{-31}
Cuprous Bromide	CuBr	5.3×10^{-9}
Cupric Carbonate	$CuCO_3$	1.4×10^{-10}
Cuprous Chloride	CuCl	1.7×10^{-6}
Cupric Hydroxide	$Cu(OH)_2$	2.2×10^{-20}
Cuprous Iodide	CuI	1.1×10^{-12}
Cupric Sulphide	CuS	6.3×10^{-36}
Ferrous Carbonate	$FeCO_3$	3.2×10^{-11}
Ferrous Hydroxide	$Fe(OH)_2$	8.0×10^{-16}
Ferric Hydroxide	$Fe(OH)_3$	1.0×10^{-38}
Ferrous Sulphide	FeS	6.3×10^{-18}
Mercurous Bromide	Hg_2Br_2	5.6×10^{-23}
Mercurous Chloride	Hg_2Cl_2	1.3×10^{-18}
Mercurous Iodide	Hg_2I_2	4.5×10^{-29}
Mercurous Sulphate	Hg_2SO_4	7.4×10^{-7}
Mercuric Sulphide	HgS	4.0×10^{-53}
Magnesium Carbonate	$MgCO_3$	3.5×10^{-8}
Magnesium Fluoride	MgF_2	6.5×10^{-9}
Magnesium Hydroxide	$Mg(OH)_2$	1.8×10^{-11}
Magnesium Oxalate	MgC_2O_4	7.0×10^{-7}
Manganese Carbonate	$MnCO_3$	1.8×10^{-11}
Manganese Sulphide	MnS	2.5×10^{-13}
Nickel Hydroxide	$Ni(OH)_2$	2.0×10^{-15}
Nickel Sulphide	NiS	4.7×10^{-5}
Lead Bromide	$PbBr_2$	4.0×10^{-5}
Lead Carbonate	$PbCO_3$	7.4×10^{-14}
Lead Chloride	$PbCl_2$	1.6×10^{-5}
Lead Fluoride	PbF_2	7.7×10^{-8}
Lead Hydroxide	$Pb(OH)_2$	1.2×10^{-15}
Lead Iodide	PbI_2	7.1×10^{-9}
Lead Sulphate	$PbSO_4$	1.6×10^{-8}
Lead Sulphide	PbS	8.0×10^{-28}
Stannous Hydroxide	$Sn(OH)_2$	1.4×10^{-28}
Stannous Sulphide	SnS	1.0×10^{-25}
Strontium Carbonate	$SrCO_3$	1.1×10^{-10}
Strontium Fluoride	SrF_2	2.5×10^{-9}
Strontium Sulphate	$SrSO_4$	3.2×10^{-7}
Thallous Bromide	TlBr	3.4×10^{-6}
Thallous Chloride	TlCl	1.7×10^{-4}
Thallous Iodide	TlI	6.5×10^{-8}
Zinc Carbonate	$ZnCO_3$	1.4×10^{-11}
Zinc Hydroxide	$Zn(OH)_2$	1.0×10^{-15}
Zinc Sulphide	ZnS	1.6×10^{-24}

Example 8.23

Determine the solubility of AgCl, $Fe(OH)_3$, Hg_2Br_2 and Ag_2SO_4 from their solubility product constants given in Table 8.7. Calculate the molarities of the individual ions and also the solubilities of the salts in g L^{-1}.

Solution

For AgCl: $K_{sp} = 1.8 \times 10^{-10}$, hence

$S/M = (1.8 \times 10^{-10})^{1/2} = 1.34 \times 10^{-5}$

$[Ag^+] = [Cl^-]$; $S = 1.34 \times 10^{-5}$ mol L^{-1} and S for AgCl in g L^{-1}

$= 1.34 \times 10^{-5}$ mol $L^{-1} \times 143.35$ g mol^{-1}

$= 1.92 \times 10^{-3}$ g L^{-1}.

For ferric hydroxide: $K_{sp} = 1.0 \times 10^{-38}$ and

$S/M = (1.0 \times 10^{-38}/3^3)^{1/4}$; $S = 1.39 \times 10^{-10}$

$[Fe^{3+}] = 1.39 \times 10^{-10}$ mol L^{-1} and

$[OH^-] = 3S = 4.17 \times 10^{-10}$ mol L^{-1}

and S for ferric hydroxide in g L^{-1}

$= 1.39 \times 10^{-10}$ mol $L^{-1} \times 106.85$g mol^{-1}

$= 1.40 \times 10^{-8}$g L^{-1}

For mercurous bromide:

$K_{sp} = 5.6 \times 10^{-23}$ but in mercurous bromide the mercurous ion is Hg_2^{2+} and therefore we have

$S/M = \{5.6 \times 10^{-23} (2)^2\}^{1/3}$; $S = 2.41 \times 10^{-8}$ mol L^{-1} and S for mercurous bromide in g L^{-1}

$= 2.41 \times 10^{-8}$ mol $L^{-1} \times 360.4$g mol^{-1}

$= 8.68 \times 10^{-6}$g L^{-1}

$[Hg_2^{2+}] = 2.41 \times 10^{-8}$ M, $[Br^-] = 4.82 \times 10^{-8}$ M

For silver sulphate: $K_{sp} = 1.4 \times 10^{-5}$ and

$S/M = \{1.4 \times 10^{-5}/2^2\}^{1/3}$; $S = 1.52 \times 10^{-2}$ mol L^{-1} and S for silver sulphate (in g L^{-1})

$= 1.52 \times 10^{-2}$ g $mol^{-1} \times 311.8$ g mol^{-1}

$= 4.74$ g L^{-1} and we have

$[Ag^+] = 2S = 3.04 \times 10^{-2}$ mol L^{-1} and $[SO_4^{2+}]$

$= 1.52 \times 10^{-2}$ mol L^{-1}

Example 8.24

How many grams of potassium bromide can be added to 1 litre of 0.05 M solution of sliver nitrate just to start the precipitation of silver bromide?

Solution

For silver bromide, $K_{sp} = [Ag^+]\,[Br^-] = 5.0 \times 10^{-13}$

The precipitation of silver bromide will start only when the product of the concentrations of silver and bromide ions exceeds the solubility product constant for silver bromide. Let us suppose the precipitation starts when 'x' g of potassium bromide have been added to one litre of solution. Then

$[Br^-]=[KBr] = x/\text{molar mass of KBr} = x/120$ while $[Ag^+] = [AgNO_3] = 0.05$

We can find the value of 'x' by solving the equation:

$(x/120)\,(0.05) = 5 \times 10^{-13}$ or $x = 1.2 \times 10^{-9}$ g

It may be mentioned that a saturated solution of AgBr is sufficient to kill harmful bacteria in drinking water. The tablets of suitable silver salts are used by soldiers and hunters to purify raw water in case of emergency.

8.5.2 Common Ion Effect on Solubility of Ionic Salts

It is expected from Le Chatelier's principle (*Unit –7*) that if we increase the concentration of any one of the ions, it should combine with the ion of its opposite charge and some of the salt will be precipitated till once again $K_{sp} = Q_{sp}$. Similarly if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentrations of both the ions till once again $K_{sp} = Q_{sp}$. This is applicable even to soluble salts like sodium chloride except that due to higher concentration of the ions, we use their activities instead of their molarities in the expression for Q_{sp}. Thus if we take a saturated solution of sodium chloride and pass HCl gas through it, then sodium chloride is precipitated due to increased concentration (activity) of chloride ion available from the dissociation of HCl. Sodium chloride thus obtained is of very high purity and we can get rid of impurities like sodium and magnesium sulphates. The common ion effect is also used for almost complete precipitation of a particular ion as its sparingly soluble salt, with very low value of solubility product for gravimetric estimation. Thus we can precipitate silver ion as silver chloride, ferric ion as its hydroxide and barium ion as its sulphate for gravimetric estimations.

Example 8.25

Determine the solubility of barium sulphate in 0.05 M in barium chloride solution. The solubility product constant of barium sulphate may be taken from Table 8.7.

Solution

Let the solubility of barium sulphate be equal to *S*, then the concentration of barium ion, $Ba^{2+} = 0.05 + S$ while that of sulphate ion, $SO_4^{2-} = S$. We can determine the value of *S* by solving the equation:

$[Ba^{2+}][SO_4^{2-}] = (0.05 + S)\,(S) = K_{sp} = 1.1 \times 10^{-10}$.

As the value of *S* is much smaller, we can neglect it compared to 0.05 and the simplified equation:

$0.05\,S = 1.1 \times 10^{-10}$ gives us $S = 2.2 \times 10^{-9}$. It can be seen that our assumption about molar solubility, *S* being small (2.2×10^{-9}), is correct in neglecting it compared to 0.05 M.

The solubility of salts of weak acid increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increase the solubility of the salt so that $K_{sp} = Q_{sp}$. We have to satisfy two equilibria simultaneously i.e.

$K_{sp} = [M^+][X^-]$ and $[X^-]/[HX] = K_a/[H^+]$ and at a particular value of $[H^+]$ we have

$[X^-]/\{[X^-] + [HX]\} = f = K_a/(K_a + [H^+])$ and it can be seen that 'f' decreases as pH decreases. If *S* is the solubility of the salt at a given pH then

$K_{sp} = [S]\,[fS] = S^2\,\{K_a/(K_a + [H^+])\}$ and

$$S = \{K_{sp}\,[H^+] + K_a)/K_a\}^{1/2} \qquad (8.33)$$

Thus solubility S increases with increase in $[H^+]$ or decrease in pH.

SUMMARY

We have noted that all the electrolytes are acids, bases, and salts and the conduction of electricity by their aqueous solutions is due to anions and cations produced by the dissociation or ionization of electrolytes in aqueous solution. The strong electrolytes are completely dissociated. In *weak electrolytes*, there is equilibrium between the ions and the unionized electrolyte molecules. According to Arrhenius, acids give hydrogen ions while bases produce hydroxyl ions in their aqueous solutions. Brönsted-Lowry on the other hand, defined an acid as a proton donor and a base as a proton acceptor. When such an acid reacts with a base, it produces its conjugate base and a conjugate acid corresponding to the base with which it reacts. Thus a conjugate pair of acid-base differ only by one proton. Lewis further generalized the definition of an acid as an electron pair acceptor and a base as an electron pair donor. The expressions for ionization (equilibrium) constants of weak acids (K_a) and weak bases (K_b) are developed using Arrhenius definitions. The degree of ionization and its dependence on concentration and common ion are discussed. The pH scale (pH = -log[H^+]) for the hydrogen ion concentration (activity) has been introduced and extended to other quantities (pOH = -log [OH^-] ; pK_a = -log [K_a] ; pK_b = - log [K_b]; and pK_w = -log [K_w] etc.). The ionization of water has been considered and we note that the equation:pH + pOH = pK_w is always satisfied. Expressions for the hydrolysis constants of the salts of weak acid – strong base ($K_h = K_w / K_a$), strong acid-weak base ($K_h = K_w / K_b$) and weak acid-weak base ($K_h = K_w / K_a K_b$) are derived. Methods for the calculations of the degree of hydrolysis of the salts and the pH of their solutions and their dependence on concentration have been developed. The methods for calculating pH during various stages of acid-base titration have been discussed in detail for different cases and their importance in the choice of a suitable indicator, so that the end point (observed by the colour change of the indicator) is as near to the equivalence point (corresponding to the stochiometric amounts of acid and base present in the mixture) for best quantitative estimation are discussed. We also note that some acids on ionization can give two or more than two protons per molecule of the acid. Such acids are called *polybasic* or *polyprotic* acids. Similarly we have *polyacidic bases* which give two or more than two hydroxyl ions per molecule of the base. The definition of buffer solutions, the method of their preparation and their importance are discussed briefly. The solubility equilibrium of sparingly soluble salts is discussed and the equilibrium constant is introduced as solubility product constant (K_{sp}). Its relationship with solubility of the salt is established. The conditions of precipitation of the salt from their solutions or their dissolution in water is worked out. The role of common ion and the solubility of sparingly soluble salts is also discussed.

SUGGESTED ACTIVITIES FOR STUDENTS REGARDING THIS UNIT

(a) The student may use pH paper in determining the pH of fresh juices of various vegetables and fruits, soft drinks, body fluids and also that of water samples available.
(b) The pH paper may also be used to determine the pH of different salt solutions and from that he/she may determine if these are formed from strong/weak acids and bases.
(c) They may prepare some buffer solutions by mixing the solutions of sodium acetate and acetic acid and determine their pH using pH paper.
(d) They may be provided with different indicators to observe their colours in solutions of varying pH.
(e) They may perform some acid base titrations using indicators.
(f) They may observe common ion effect on the solubility of sparingly soluble salts.
(g) If pH meter is available in their school, they may measure the pH with it and compare the results obtained with that of the pH paper.

EXERCISES

8.1 What is meant by the conjugate acid base pair? Find the conjugate acid/base for the following species:
HNO_2, CN^-, $HClO_4$, F^-, OH^-, CO_3^{2-}, and S^{2-}.

8.2 Which of the followings are Lewis acids?
H_2O, BF_3, H^+, and NH_4^+.

8.3 The ionization constants of HF, HCOOH and HCN at 298 K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

8.4 The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenate?

8.5 The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1 M solution and how will this concentration be effected if the solution is 0.1 M in HCl also. If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

8.6 Assuming complete dissociation calculate the pH of the following solutions:
(a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 KOH.

8.7 Calculate the pH of the following solutions:
(a) 2 g of TlOH dissolved in water to give 2 litre of solution.
(b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.
(c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.
(d) 1 ml of 13.6 M HCl is diluted with water to give 1 litre of solution.

8.8 Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:
(a) Human muscle-fluid 6.83 (b) Human stomach fluid 1.2 (c) Human blood 7.38
(d) Human saliva 6.4.

8.9 The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.

8.10 If 0.561 KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

8.11 The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

8.12 The ionization constant of propionic acid is 1.32×10^{-5}. Calculate the degree of ionization of the acid in its 0.05 M solution and also its pH. What will be its degree of ionization if the solution is 0.01 in HCl also?

8.13 The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

8.14 The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

8.15 A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.

8.16 Predict if the solutions of the following salts are neutral, acidic or basic:
NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF.

8.17 The ionization constant of chloroacetic is 1.35×10^{-3}. What will be pH of 0.1 M acid and its 0.1 M sodium salt solution?

8.18 Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

8.19 Calculate the pH of the mixture formed by the addition of 5, 9, 9.5, 9.9, 9.95, 10, 10.05, and 10.1 mL of 0.5 M KOH solution to 100 mL of 0.05 HBr solution. What will be the most suitable indicator for this titration?

8.20 Calculate the pH of the resultant mixtures:
(a) 10 mL of 0.2 M $Ca(OH)_2$ + 25 mL of 0.1 M HCl.
(b) 10 mL of 0.01 M H_2SO_4 + 10 mL of 0.01 M $Ca(OH)_2$.
(c) 10 mL of 0.1 M H_2SO_4 + 10 mL of 0.1 M KOH.

8.21 The pH of an enzyme catalyzed reaction has to be monitored between pH 7 & 8. What indicator should be used to monitor and control the pH of the reaction? (Please see Table 8.5)

8.22 The pK_{In} of an indicator is 10.5. For which pH transition range is the indicator most suitable.

8.23 Benzoic acid is monobasic and when 1.22 g of its pure sample after dissolution in distilled water is titrated against a base it uses 50 mL of 0.2 M NaOH. Calculate the molar mass of benzoic acid.

8.24 Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298 K from their solubility product constants given in Table 8.7. Determine also the molarities of individual ions.

8.25 The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

8.26 Equal volumes of 0.002 M solutions of sodium iodate and copper chlorate are mixed together. Will it lead to precipitation of copper iodate? For copper iodate $K_{sp} = 7.4 \times 10^{-8}$.

8.27 The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

8.28 What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide. For iron sulphide $K_{sp} = 6.3 \times 10^{-18}$.

8.29 What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298 K. For calcium sulphate, K_{sp} is 9.1×10^{-6}.

8.30 The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19}M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. In which solutions precipitation will take place. (Please consult Table 8.7)

UNIT 9

REDOX REACTIONS

Objectives

After studying this Unit, you will be able to

- learn about redox reactions in which oxidation and reduction reactions take place simultaneously.
- understand the meaning of oxidation, reduction, oxidant (oxidizing agent) and reductant (reducing agent).
- understand redox reactions and mechanism of redox processes by transfer of electron from reductant to oxidant.
- determine the oxidation number of an element in a compound and identify oxidant and reductant in a reaction on the basis of change in oxidation number.
- balance chemical equations using (i) oxidation number and (ii) half reaction or ion-electron methods.
- learn the concept of redox couple and the construction and functioning of a galvanic cell.

"Where there is a oxidation, there is always reduction – Chemistry is essentially a study of redox systems."

In the previous Unit we studied neutralization reactions. In these reactions, a proton is transferred from the acid to the base and if the base is a hydroxide of alkali or alkaline earth metal, the reaction leads to the formation of salt and water. In this Unit we shall consider another very important class of reactions called **Redox Reactions.** A large number of chemical and biological reactions fall in this category. Burning of different types of fuels for obtaining energy for domestic, transport or industrial purpose; electrochemical processes like manufacturing of caustic soda; digestion of food in animals; photosynthesis by plants; corrosion of metals; and operation of dry and wet batteries are diverse examples of redox reactions.

9.1 ROLE OF ELECTRONS IN REDUCTION-OXIDATION REACTIONS

In redox reactions one reactant called **reductant or reducing agent** is oxidized while the other reactant called **oxidant or oxidizing agent** is reduced. Originally oxidation of a substance was defined as the addition of oxygen to it. Due to presence of oxygen in the atmosphere (~20%) many elements combine with it. In fact the most common occurrence of elements on the earth is in the form of their oxides. Later on removal of hydrogen from a substance was also considered as oxidation. The following reactions represent oxidation processes according to this limited definition of oxidation:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s) \quad (9.1)$$

$$2H_2S(g) + O_2(g) \rightarrow 2S(s) + 2H_2O(l) \quad (9.2)$$

In reaction (9.1) magnesium is oxidized by addition of

oxygen to it while in reaction (9.2) hydrogen sulphide is oxidized by removal of hydrogen from it. It was only natural to extend the term oxidation for reactions similar to (9.1) to those not involving oxygen but other electronegative elements. The oxidation of magnesium with fluorine, chlorine and sulphur etc. takes place according to the following reactions:

$$Mg(s) + F_2(g) \rightarrow MgF_2(s) \quad (9.3)$$

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s) \quad (9.4)$$

$$Mg(s) + S(s) \rightarrow MgS(s) \quad (9.5)$$

In the above oxidation reactions, as in the reaction (9.1), Mg is converted into Mg^{2+} ion and in the process it loses 2 electrons. Therefore, **oxidation in general can be defined as a reaction in which electrons are lost or removed.**

The term reduction was initially introduced for the processes in which metal oxides were converted into metals by their reactions with hydrogen, carbon or other metals. Carbon monoxide is used in the reduction of ferric oxide to iron. A few reduction reactions by such substances are given below:

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l) \quad (9.6)$$

$$2CuO(s) + C(s) \rightarrow 2Cu(s) + CO_2(g) \quad (9.7)$$

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \quad (9.8)$$

In reactions (9.1), (9.3), (9.4) and (9.5) magnesium is oxidized by different electronegative substances but one thing is common in all these reactions, i.e. magnesium has lost two electrons to become magnesium ion. Therefore, **the general definition of oxidation is loss of electrons and the reactant like magnesium that loses electron acts as a reductant or reducing agent.** Similarly it is evident from reactions (9.6) to (9.8) that in each case the metal ions in the form of their oxides have accepted electrons from the reducing agents and thus **reduction in general means acceptance of electron(s) by a reactant and it acts as an oxidant or oxidizing agent.** Thus in the reactions (9.1), (9.3) and (9.4), oxygen, fluorine and chlorine all act as oxidizing agents by accepting electrons and these are converted to their respective ions (O^{2-}, F^-, Cl^-). Similarly hydrogen, carbon and carbon monoxide in the reactions (9.6) to (9.8) act as reducing agents. **It is thus obvious that in a redox reaction, oxidant is reduced by accepting electrons and reductant is oxidized by losing electrons.** It may be again emphasized that oxidation and reduction in any redox reaction have to occur simultaneously. It is obvious from the reactions (9.1) to (9.8) that while one reactant is oxidized the other is reduced. It may be mentioned that the role of a substance to act as an electron donor or acceptor and hence as a reductant or oxidant depends upon electron accepting or donating capacity of the other reactant. This is apparent from the experimental set up in Fig.9.1. In the beaker A, we have a zinc rod dipped in a solution of copper sulphate and in beaker B we have a copper rod dipped in a solution of silver nitrate.

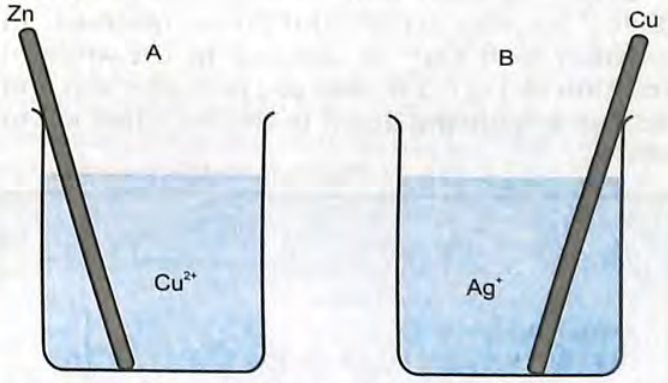


Fig.9.1 *In beaker A, metallic zinc dissolves and is oxidized to zinc ion and copper ion is reduced to metallic copper while in beaker B, metallic copper dissolves and is oxidized to copper ion and silver ion is reduced to metallic silver*

After a few minutes we observe that in beaker A, zinc rod dissolves partially and its surface is coated with copper metal. This is because the following reaction takes place:

$$Zn(s) + Cu^{2+}(aq) + SO_4^{2-}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) + SO_4^{2-}(aq)$$

In the above reaction sulphate ion does not participate and we may now write the reaction as given below:

Oxidation(loss of $2e^-$)

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad (9.9)$$

Reduction (gain of $2e^-$)

In this reaction zinc acts as a reducing agent and is able to reduce Cu^{2+} to Cu by transferring

two electrons. Here copper ion acts as an oxidizing agent. On the other hand in beaker B, copper dissolves partially and metallic silver is deposited from silver nitrate solution. In this case the following reaction takes place:

$$Cu(s) + 2Ag^+(aq) + 2NO_3^-(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s) + 2\,NO_3^-(aq)$$

In the above reaction nitrate ion is inert and the reaction may be written as:

$$\underset{\text{Oxidation (loss of } 2e^-)}{Cu(s)} + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + \underset{\text{Reduction (gain of } 2e^-)}{2Ag(s)} \quad (9.10)$$

It can be seen that in reactions (9.9) and (9.10), the roles of Cu^{2+} and Cu are reversed. In reaction (9.9) Cu^{2+} is reduced to Cu while in reaction (9.10) Cu is oxidized to copper ion and acts as a reducing agent to reduce silver ion to silver.

Example 9.1

Identify the oxidant and the reductant in the following reactions:

(a) $Zn(s) + \frac{1}{2} O_2(g) \rightarrow ZnO(s)$.

(b) $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$.

Solution

In reaction (a) Zn donates electrons to O to give zinc and oxide ions. Therefore, Zn acts as a reducing agent while oxygen acts as an oxidizing agent.

In reaction (b) Zn transfers its electrons to H^+ and therefore, zinc acts as a reducing agent and H^+ acts as an oxidizing agent.

The concept of oxidation and reduction in terms of electron transfer can be applied easily to ionic reactions. However, in many reactions involving covalent compounds the direction of transfer of electrons from one reactant to other is not very obvious from the chemical equations. For example in the reaction:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \quad (9.11)$$

all the reactants and the product are covalent compounds. In the product molecule HCl, electron pair is shared between hydrogen and chlorine atoms and the electron is not completely transferred from hydrogen to chlorine atom. Yet (9.11) is a redox reaction because in HCl molecule chlorine atom has higher electron density and there is a partial transfer of electronic charge from hydrogen atom to chlorine atom and we say that hydrogen is a reductant and chlorine is an oxidant. In the same way in the reaction:

$$CH_4(g) + 4F_2(g) \rightarrow CF_4(g) + 4HF(g) \quad (9.12)$$

CH_4 acts as a reducing agent while fluorine acts as an oxidizing agent. The transfer of electron in redox reactions involving covalent compounds is not quite obvious. In order to identify oxidant and reductant in a redox reaction, the concept of oxidation number has been found quite useful and it has also been found meaningful in balancing chemical equations representing complex redox reactions.

9.2 OXIDATION NUMBER

In the previous section, we noted that the electron pair in the covalent bond in HCl is not equally shared between hydrogen and chlorine atoms. There is higher electron density on chlorine atom (more electronegative) so that it has a small negative charge while hydrogen atom (less electronegative) has a small positive charge as shown below:

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

Such charge densities on atoms can be calculated in principle by the quantum mechanical methods but these values are not readily available for even common substances. Therefore, a more practical method using *oxidation number* method has been developed for the study of redox reactions. In this method it is always assumed that there is a complete transfer of electron from a less electronegative atom to more electronegative atom. It must be emphasized that this assumption is made for book-keeping purpose only and it will become obvious from the discussion later in this section that it leads to simple description of the redox reaction.

Oxidation number defines the state of oxidation of an element in a compound calculated according to a set of rules formulated on the basis that electron in a covalent bond entirely belongs to the more electronegative element.

It is not always possible to remember or see easily in a compound as to which element is more electronegative and therefore a set of rules has been framed to determine the oxidation number of an element in a compound. If two or more than two atoms of an element are present in the molecular formula of a compound, the oxidation number for that element will be the average of all the atoms of that element. We now state the rules for the determination of oxidation number.

1. *Each atom in an element in any of its allotropic form is assigned an oxidation number of 0.*

Thus hydrogen atom in H_2, oxygen atom in O_2 or O_3, carbon atom in diamond, helium atom in He, P atom in molecule P_4 and S atom in molecule S_8 etc. all have oxidation number equal to zero.

2. *Oxidation number of an atom in its charged monoatomic ion is equal to the charge on the ion.*

Thus in monoatomic ions like Na^+, Mg^{2+}, Al^{3+}, Cl^-, and S^{2-}, the oxidation number of sodium, magnesium, aluminum, chlorine and sulphur atoms are +1, +2, +3, -1 and -2 respectively.

3. *The oxidation number of elements in their compounds or compound ions is obtained using the following rules.*

   (a) Hydrogen is assigned oxidation number +1 and oxygen is assigned oxidation number –2 in almost all their compounds. The exception for hydrogen is in metal hydrides (KH, MgH_2, CaH_2, LiH etc.) where the oxidation number for hydrogen is –1. Exceptions for oxygen occur in peroxides and fluorides. In H_2O_2, Na_2O_2 the oxidation number of oxygen is –1. In case of oxygen fluoride like OF_2, its oxidation number is +2.

   (b) The most electronegative element fluorine, has oxidation number –1. For other halogens the oxidation number is generally –1 but when these are bonded to a more electronegative halogen atom or to oxygen, there are exceptions. Thus in HI the oxidation number of I is –1 but in IF_7, it is +7.

   (c) The oxidation number of alkali metals in all their compounds is +1 and for alkaline earth metals oxidation number is +2.

   (d) The algebraic sum of the oxidation number of all the atoms in a neutral molecules is 0. If the species is an ion rather than a neutral molecule, the algebraic sum of the oxidation number of the atoms in the ion must equal the charge of the ion.

The rule 3(d) is very helpful in finding the oxidation number of an atom if those of all the other atoms in the given species are known. We shall use this quite often.

By applying these rules we can find the oxidation number of any element in a molecule or an ion. It is clear that metallic elements have positive oxidation number while nonmetallic elements can have positive or negative oxidation number. The transition metals usually display several oxidation numbers. The highest oxidation number of a representative element is the group number in the older group notation of the periodic table and thus the highest value of oxidation number exhibited by an atom of an element generally increases across the periodic table. Thus in the third period the highest value of oxidation number varies from 1 to 7 as shown below :

$Na^+(1)$, $Mg^{2+}(2)$, $Al^{3+}(3)$, Si(4) as in $SiCl_4$, P(5) as in PF_5, S(6) as in SF_6, and Cl(7) as in ClO_4^-.

A term that is frequently used interchangeably with oxidation number is **Oxidation State.** Thus in H_2O, the oxidation state of hydrogen is +1 that is also its oxidation number and similarly the oxidation state of oxygen is –2. This means that the oxidation number gives the oxidation state of an element in a compound. The oxidation state of a metal in a compound according to **Stock notation** is given by putting the oxidation number as Roman numeral in parenthesis after the symbol of the metal in the molecular formula. Thus cuprous chloride and cupric chloride are written as $Cu_2(I)Cl_2$ and $Cu(II)Cl_2$. Similarly, ferrous sulphate and ferric sulphate are written as $Fe(II)SO_4$ and $Fe_2(III)(SO_4)_3$. Any change in oxidation number implies change of oxidation state. Thus change in oxidation number helps in identifying the oxidant and reductant in a redox reaction.

An increase in oxidation number corresponds to oxidation of the element in the given compound that acts as a reductant or reducing agent. Similarly a decrease in

oxidation number corresponds to reduction of the element in the compound and it behaves as an oxidant or oxidizing agent.

We shall now illustrate the application of the above rules in determining the oxidation numbers and also for identifying the reductants and oxidants in the redox reactions.

Example 9.2

Find the oxidation numbers of sulphur in the following compounds
H_2S, H_2SO_4, $S_2O_4^{2-}$, $S_2O_8^{2-}$ and HSO_3^-.

Solution

According to rule 3(d) for a neutral molecule, sum of oxidation number of all the atoms is equal to zero and for a charged species equals to the charge on the ion.

In $\mathbf{H_2S}$ the oxidation number (o.n.) of H is +1, using the sum rule 3(d) we have:

2×1 + o.n. of S = 0 or oxidation number of S is –2.

In $\mathbf{H_2SO_4}$ the oxidation number (o.n.) of H is +1, for O it is –2, and following rule 3(d) we have:

$2 \times 1 - 2 \times 4$ + o.n. of S = 0 or oxidation number of S is +6.

In $\mathbf{S_2O_4^{2-}}$ (o.n.) of O is –2; and using rule 3(d) we have:

$4 \times (-2) + 2 \times$ (o.n. of S) = -2 or oxidation number of S is +3.

In $\mathbf{S_2O_8^{2-}}$ we have one peroxide bond, therefore for two oxygen atoms oxidation number is –1 and for the other six oxygen atoms, the o.n. is –2. Now following rule 3(d) we have:

$6 \times (-2) + 2 \times (-1) \times 2$ o.n. of S = -2 or Oxidation number of S = 6.

In $\mathbf{HSO_3^-}$ o.n. for H is +1 and oxidation number of O is –2 and following rule 3(d)we have:

1 + o.n. of S + 3(-2) = -1 or Oxidation number of S = +4.

It may be noted that sulphur is in different oxidation states in different compounds. This is true in the next example also in which Cl is in different oxidation states.

Example 9.3

Find the oxidation number of Cl in HCl, HClO, ClO_4^- and Ca(OCl)Cl.

Solution

It is obvious that in **HCl** the o.n. for H is +1 and therefore for Cl it should be –1.

In **HClO,** the o.n. for H is +1 and for O is -2 and therefore for Cl it should be +1.

In $\mathbf{ClO_4^-}$, the o.n. for O is -2 and therefore for Cl it should be +7.

In **Ca(OCl)Cl,** the o.n. of Ca is +2 and that of O is –2 and following rule 3(d) we have :

$1 \times 2 + 1 \times (-2) + 2$ (o.n. of Cl) = 0 and we have o. n. of Cl = 0.

It may be mentioned here that one chlorine atom exists as chloride ion for which the oxidation number is –1 and the other chlorine atom exists as hypochlorite ion in which the oxidation number of chlorine is +1. The o.n. of Cl in the compound is the average of the oxidation numbers of all the atoms of the element. In this case the average is zero in agreement with our calculated value.

Example 9.4

Find the oxidation number of carbon in the following compounds:
CH_3OH, CH_2O, HCOOH, C_2H_2.

Solution

In all these compounds H has oxidation number +1 and O has oxidation number –2. Using rule 3(d) the values of o.n. of carbon in each of the above compounds can be determined using the following general method.

If the number of hydrogen atoms in the compound is n_H, the number of oxygen atom is n_O and the number of carbon atoms is n_C then we have:

n_H (1) $+n_O$ (-2) + n_C(o.n. of carbon) = 0

or o.n. of carbon in the compound = $\{n_O$ (2) - n_H (1) $\}/n_C$

The results for different compounds are given in table below:

Compound	n_H	n_O	n_C	o.n. of C = $\{n_O \times 2 - n_H\}/n_C$
CH_4	4	0	1	-4
CH_3OH	4	1	1	-2
CH_2O	2	1	1	0
HCOOH	2	2	1	+2
C_2H_4	4	0	2	-2
C_2H_2	2	0	2	-1

Example 9.5

Find the oxidation number of Fe in Fe_3O_4 and in $Fe(III)_4[Fe(II)(CN)_6]_3$.

Solution

In Fe_3O_4, each O has o.n = -2 and therefore we have:

4(-2) + 3 (o.n. of Fe) = 0 or the o.n. of Fe = 8/3

Actually Fe_3O_4, known as magnetic oxide of iron is a stoichiometric mixture of ferrous (FeO) and ferric (Fe_2O_3) oxides and the value 8/3 for the oxidation number is the average of all the Fe atoms in the molecule.

In the ferriferrocynide, $Fe_4[Fe(CN)_6]_3$ molecule we have 4 iron atoms with o.n. +3 and 3 iron atoms with o.n. + 2 and the o.n. of iron in the molecule is the average of all these atoms equal to 18/7.

Example 9.6

Identify the oxidant and reductant in the following reactions:

(a) $10H^+(aq) + 4Zn(s) + NO_3^-(aq) \rightarrow 4\,Zn^{2+}(aq) + NH_4^+(aq) + 3H_2O(l)$

(b) $I_2(g) + H_2S(g) \rightarrow 2HI(g) + S(s)$

Solution

In the reaction (a) there is no change in the o.n. of hydrogen and oxygen. Oxidation number of Zn changes from zero to +2 and therefore, it is oxidized and hence acts as a reductant. The oxidation number of N in nitrate ion is +5 and in ammonium ion it is –3 and therefore, it is reduced and acts as an oxidant.

In reaction (b) the oxidation number of iodine changes from 0 to –1. Therefore, it is reduced and acts as an oxidant. The oxidation number of S in hydrogen sulphide changes from –2 to 0. Therefore, it is oxidized and hence acts as a reductant.

Chemical equations corresponding to some redox reactions are quite simple and can be balanced on inspection. However, in some cases these are quite complex and it may not be easy even for an expert to balance these by simply looking at them. He has to proceed in a systematic manner to balance the chemical equations. In the next section we shall study methods for balancing chemical equation for any redox reaction.

9.3 BALANCING CHEMICAL EQUATIONS

Two methods are used for balancing chemical equations for redox reactions. The first method is based on the change in the oxidation number of the reductant and the oxidant and the second method is based on splitting the redox reaction into two half reactions one involving oxidation and the other involving reduction. Both methods work very well and choice depends on the individual using it.

9.3.1 Oxidation Number Method

The method is best explained in the following steps:

Step 1. Write the skeletal equation for all the known reactants and products of the reaction.

Step 2. Indicate the o.n. of all the atoms in each compound in the skeletal equation and ignore the atoms or groups in which there is no change of oxidation number. Now identify the atoms undergoing change in their o.n.

Step 3. Calculate the increase or decrease in the oxidation number per atom and then for the whole molecule in which it occurs. If these are not equal then multiply by suitable coefficients so that these become equal.

Step 4. Balance the chemical equation with respect to all atoms except H and O.

Step 5. Finally balance with respect to H and O atoms. For balancing for oxygen atoms add water molecules to the side deficient in it. Balancing of hydrogen atoms will depend on the medium (acidic or basic) as explained below :

(a) If we are working in an acidic medium then deficiency in hydrogen atoms can be made up by adding hydrogen ions on the side that is deficient in it.

(b) On the other hand, in a basic medium deficiency in hydrogen atoms can be made up by adding water molecules on the deficient side and adding equal number of hydroxyl ions on the other side of the equation.

Finally, the equation is balanced by cancelling common species present on both sides of the equation.

Various steps involved in the method will now be explained with the help of a few examples.

Example 9.7

Copper metal reacts with nitric acid to give cupric ions and nitrogen dioxide. Find the balanced chemical equation corresponding to this reaction.

Solution

Step 1. The skeletal equation can be written from the known reactants and products and we have:

$Cu(s) + HNO_3(aq) \rightarrow Cu^{2+}(aq) + NO_2(g)$

Step 2. We write the oxidation number of each atom in all the compounds in the skeletal equation. These are shown in bold below each atom.

$$\begin{array}{lccccc} & Cu(s) & + & HNO_3(aq) & \rightarrow & Cu^{2+}(aq) + NO_2(aq) \\ \text{o.n.} & \mathbf{0} & & \mathbf{1,5,-2} & & \mathbf{2} \qquad \mathbf{4,-2} \end{array}$$

Step 3. It can be seen that there is no change in the oxidation number of oxygen but that of Cu increases by 2 and that of nitrogen decreases by 1. Therefore, we can say that HNO_3 is oxidant and Cu is reductant. Now to make the increase and decrease of oxidation number for reductant and oxidant equal, we should multiply HNO_3 by 2. We have now:

$Cu(s) + 2\,HNO_3(aq) \rightarrow Cu^{2+}(aq) + NO_2(g)$

Step 4. In order to balance for N atom, we multiply NO_2 by 2 and we get:

$Cu(s) + 2\,HNO_3(aq) \rightarrow Cu^{2+}(aq) + 2\,NO_2(g)$

Step 5. All other atoms are already balanced except for H and O and for balancing for oxygen we add 2 water molecules on the right hand side.

$Cu(s) + 2HNO_3(aq) \rightarrow Cu^{2+}(aq) + 2\,NO_2(g) + 2H_2O(l)$

The reaction takes place in acidic medium and therefore the equation is now balanced by adding H^+ on the left hand side and we have the balanced equation:

$2\,H^+(aq) + Cu(s) + 2HNO_3(aq) \rightarrow Cu^{2+}(aq) + 2\,NO_2(g) + 2H_2O(l)$

The equation is now balanced in all respects.

Example 9.8

Dichromate ion in aqueous acidic medium reacts with ferrous ion to give ferric and chromic ions. Write the balanced chemical equation corresponding to the reaction.

Solution

Step 1. The reaction takes place in aqueous acidic medium and we can write the skeletal equation:

$$\begin{array}{lccccc} & Cr_2O_7^{2-}(aq) & + & Fe^{2+}(aq) & \rightarrow & Cr^{3+}(aq) + Fe^{3+}(aq) \\ & \mathbf{6} & & \mathbf{2} & & \mathbf{3} \qquad \mathbf{3} \end{array}$$

Step 2. The oxidation number of Cr in dichromate ion is +6 and it changes to +3 in chromic ion. The oxidation number of Fe^{2+} is 2 and that of Fe^{3+} is 3. Therefore dichromate acts as an oxidant and ferrous ion as reductant.

Step 3. The oxidation number of chromium atom decreases by 3 and for dichromate ion containing 2 chromium ions the total decrease of oxidation number is 6. The oxidation number of iron increases by 1. In order to equalize the increase and decrease in the oxidation number of the oxidant and the reductant, we must multiply by suitable coefficients and we have:

$Cr_2O_7^{2-}(aq) + 6\,Fe^{2+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$

Step 4. Now balancing with respect to all other atoms except H and O we have:

$Cr_2O_7^{2-}(aq) + 6\,Fe^{2+}(aq) \rightarrow 2\,Cr^{3+}(aq) + 6\,Fe^{3+}(aq)$

Step 5. We add 7 water molecules to the right hand side for balancing with respect to oxygen atoms. The reaction takes place in acidic medium therefore for balancing with respect to H atom we add 14 hydrogen ions on the left hand side and we obtain the balanced equation :

$14H^+(aq) + Cr_2O_7^{2-}(aq) + 6\,Fe^{2+}(aq) \rightarrow 2\,Cr^{3+}(aq) + 6\,Fe^{3+}(aq) + 7\,H_2O(l)$

Example 9.9

Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced chemical equation for the reaction.

Solution

Step 1. We first write the skeletal equation :

$$\begin{array}{lccccc} & MnO_4^-(aq) & + & Br^-(aq) & \rightarrow & MnO_2(aq) + BrO_3^-(aq) \\ & \mathbf{7} & & \mathbf{-1} & & \mathbf{4} \qquad \mathbf{5} \end{array}$$

Step 2. The oxidation numbers of oxidant and reductant atoms are given in bold in the above equation. It can be seen that permanganate ion is the oxidant and bromide ion is the reductant.

Step 3. The oxidation number of Mn decreases from 7 to 4 (i.e. decrease of 3) and that of Br increases from –1 to 5 (i.e. increase of 6). In order to have equal increase in oxidation number of reductant (bromide ion) and decrease in the oxidation number of oxidant (permanganate ion) we should multiply permanganate ion by coefficient 2 and balancing for other atoms we have:

$2MnO_4^-(aq) + Br^-(aq) \rightarrow 2\,MnO_2(aq) + BrO_3^-(aq)$

Step 4. Now balancing for oxygen atom we add one water molecule on the right hand side

$2MnO_4^-(aq) + Br^-(aq) \rightarrow 2\,MnO_2(aq) + BrO_3^-(aq) + H_2O$

Step 5. As the reaction takes place in basic medium for balancing for 2 hydrogen atoms we add 2 water molecules on the left hand side and two hydroxyl ions on the right hand side giving:

$2\,MnO_4^-(aq) + Br^-(aq) + 2H_2O(l) \rightarrow 2\,MnO_2(aq) + BrO_3^-(aq) + H_2O(l) + 2OH^-(aq)$

It can be seen that one water molecule can be cancelled from both sides and we finally obtain the balanced equation:

$2\,MnO_4^-(aq) + Br^-(aq) + H_2O(l) \rightarrow 2\,MnO_2(aq) + BrO_3^-(aq) + 2OH^-(aq)$

9.3.2 Half Reaction Method

In this method first of all we identify the oxidant and the reductant in the skeletal equation and then we split the redox reaction in two half reactions corresponding to oxidation and reduction. The balancing of the equation is carried out systematically in various steps outlined below.

Step 1. Write the skeletal equation and identify the reductant and the oxidant.

Step 2. Write half reactions separately for oxidation and reduction.

Step 3. Balance the half reactions with respect to atoms including O and H atoms as described in the previous method. Here we also balance the charge and if necessary these be balanced by addition of electrons on either side of the equation for both the half reactions.

Step 4. Multiply the half reaction equations by appropriate coefficients so that the number of electrons involved in both of the equation is same. Add the two equations and cancel the electrons and other common species on both sides.

We shall now illustrate the method by the following examples:

Example 9.10

Permanganate ion reacts with ferrous ion in acid medium to give Fe^{3+} and Mn^{2+} ions. Write the balanced chemical equation for the reaction.

Solution

Step 1 and 2. The skeletal equation here is:

$MnO_4^-(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$

From the above equation, it is obvious that permanganate ion is reduced (o.n. of Mn changes from 7 to 2) and ferrous ion is oxidized (o.n. of Fe changes from 2 to 3). We now write the two half reactions.

Reduction Half: $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$
Oxidation Half: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

Step 3. It can be seen that the half reactions are already balanced with respect to other atoms and now balancing with respect to oxygen atom by adding water molecules and for hydrogen by adding hydrogen ion (acidic medium) we have:

Reduction Half : $MnO_4^-(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ (a)
Oxidation Half : $Fe^{2+}(aq) \rightarrow Fe^{+3}(aq)$ (b)

Step 4. It can be seen that in the reduction reaction (a), the sum of the charges on left hand side is +7 while on the right hand side is +2, therefore, we can balance the charges by adding 5 electrons on the left hand side. Similarly in the oxidation reaction (b), the charges can be balanced by adding electron on the right hand side.

Reduction Half : $MnO_4^-(aq) + 8H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ (a)

Oxidation Half :

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + 1\,e^-$ (b)

As expected it can be seen above that electrons are required in the reduction reaction while these are given up in the oxidation reaction. Since these half reactions take place simultaneously, the number of electrons required in the reduction reaction should be

equal to the number of electrons released in the oxidation reaction. This can be achieved by multiplying the half reactions by suitable coefficients. In this case we need to multiply only the oxidation half reaction by 5. The final step is the addition of both the equations and we get the balanced equation after cancellation of electrons on both sides. Thus we have :

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$
$$5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$$

Adding both half equations and cancelling the electrons on both sides, we get the balanced equation:

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

Student's Activity

Prepare solution of potassium permanganate and take the solution in different test tubes. Add dilute sulphuric to some of these tubes and add solutions of some reducing agents like sodium sulphite, oxalic acid and ferrous sulphate and note down the change in the colour and explain the observations in terms of redox reactions. Repeat the above experiment with potassium dichromate solution instead of potassium permanganate solution.

Example 9.11

In passing chlorine gas through a concentrated solution of alkali we get chloride and chlorate ions. Obtain balanced chemical equation for this reaction.

Solution

Step 1. The skeletal equation is:

$$Cl_2(aq) + OH^-(aq) \rightarrow Cl^-(aq) + ClO_3^-(aq)$$

It can be seen that Cl atom has oxidation number 0 in chlorine gas while it is –1 in chloride ion and +5 in chlorate ion. Therefore chlorine gas undergoes both oxidation and reduction simultaneously and will be involved in both the half reactions[1].

Step 2. The two half reactions can be written as:

Reduction Half : $Cl_2(g) \rightarrow Cl^-(aq)$
Oxidation Half : $Cl_2(g) \rightarrow ClO_3^-(aq)$

Step 3. Balancing for all other atoms except O and H we obtain :

Reduction Half : $Cl_2(g) \rightarrow 2Cl^-(aq)$
Oxidation Half : $Cl_2(g) \rightarrow 2ClO_3^-(aq)$

We balance for oxygen atom by adding water molecules on the deficient side and obtain:

Reduction Half : $Cl_2(g) \rightarrow 2Cl^-(aq)$
Oxidation Half : $Cl_2(g) + 6H_2O(l) \rightarrow 2ClO_3^-(aq)$

The reaction takes place in alkaline medium and, therefore, for balancing of hydrogen atom we add water molecules on the deficient side and equal number of hydroxyl ion on the opposite side :

Reduction Half: $Cl_2(g) \rightarrow 2Cl^-(aq)$

Oxidation Half : $Cl_2(g) + 6H_2O(l) + 12OH^-(aq) \rightarrow 2ClO_3^-(aq) + 12H_2O(l)$

Balancing charges by adding electrons and cancelling molecules common on both sides we obtain

Reduction Half : $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

Oxidation Half : $Cl_2(g) + 12OH^-(aq) \rightarrow 2ClO_3^-(aq) + 6H_2O(l) + 10e^-$

Multiplying the reduction half by 5 to have the same number of electrons in the two half reactions and adding we obtain:

$$2Cl_2(g) + 12OH^-(aq) \rightarrow 2Cl^-(aq) + 2ClO_3^-(aq) + 6H_2O(l)$$

The above equation is balanced but it does not have the smallest stoichiometric coefficients. This can be achieved by dividing both sides by 2 leading to :

$$Cl_2(g) + 6OH^-(aq) \rightarrow Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$$

It is clear from the above examples that while splitting the reaction into reduction and oxidation half reactions, the charges of ions in these half reactions have to be balanced by adding electrons. The method is, therefore, also known as **ion-electron method.** In the next

1 *The reactions in which a species disproportionates into two oxidation states (lower and higher) are called disproportionation reactions. You will study this type of reactions in greater details while studying the chemistry of elements.*

section we shall see how such half reactions can be made to take place in an electrochemical cell.

9.3.3 Stoichiometry of Redox Reactions

In general, in a chemical reaction described by the balanced chemical equation :

$$a\,A + b\,B + \text{——} \rightarrow c\,C + d\,D + \text{——}$$

A, B ... are the reactants and C, D ... are the products. The coefficients a, b, c and d are known as stoichiometric coefficients. These indicate the number of moles of the reactants used and the number of moles of the products obtained in the reaction. In the preceding sections we have learnt to balance the chemical equations for the redox equations and obtain the stoichiometric coefficients of all the reactants and products. These coefficients must be kept in mind in all the stoichiometric calculations for the redox reactions. Such calculations are quite important in volumetric titrations based on redox reactions. The acidic permanganate is used to estimate ferrous ion. If we use $KMnO_4$ and $FeSO_4.7H_2O$ as the reactants then we know that for one mole of potassium permanganate we use 5 moles of ferrous sulphate according to the balanced stoichiometric equations. This fact was taken into account earlier by introducing the concept of equivalent weight and normality. However, in view of the more acceptable **mole concept,** *calculations are done on the basis of mole concept and molarity of the solution* (Unit-1).

Volumetric titrations based on redox reactions are carried out routinely in chemical laboratories. If we know the molarities of the reductant and oxidant and their volumes used in titration and n_1 and n_2 are their stoichiometric coefficients then it is possible to use the equation

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$ for volumetric estimation.

For example, in the titration of $FeSO_4$ with $KMnO_4$ the balanced chemical equation is:

$$10\,FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

If $FeSO_4$ is reagent '1' and $KMnO_4$ is reagent 2 then this equation becomes

$$\frac{M_1V_1}{10} = \frac{M_2V_2}{2} \quad \text{or} \quad \frac{M_1V_1}{5} = \frac{M_2V_2}{1}$$

and can be used to calculate the unknown quantity if other three quantities are known.

9.4 ELECTROCHEMICAL CELLS

In the experiment corresponding to reaction (9.9), we observed that if zinc rod is dipped in copper sulphate solution the redox reaction takes place and during the reaction, zinc is oxidized to zinc ions and copper ions are reduced to metallic copper due to direct transfer of electrons from zinc to copper ion. During this reaction heat is also evolved. Now we modify the experiment in such a manner that for the same redox reaction transfer of electrons takes place indirectly and the heat of the reaction is converted into electrical energy. This necessitates the separation of zinc metal from copper sulphate solution. We take copper sulphate solution in a beaker and put a copper strip or rod in it. We also take zinc sulphate solution in another beaker and put a zinc rod or strip in it. No reaction takes place in either of the beakers and at the interface of the metal and its salt solution in each beaker both the reduced and oxidized forms of the same species are present. These represent the species in the reduction and oxidation half reactions. **A Redox Couple is defined as having together the oxidized and reduced forms of a substance taking part in an oxidation or reduction half reaction.**

This is represented by separating the oxidized form from the reduced form by a vertical line or a slash representing an interface (e.g. solid/solution). For example in this experiment the two redox couples are represented as Zn^{2+}/Zn and Cu^{2+}/Cu. In both cases, oxidized form is put before the reduced form. Now we put the beaker containing copper sulphate solution on the right hand side of the beaker containing zinc sulphate solution (Fig. 9.2). We connect solutions in two beakers by a salt bridge (a U-tube containing a solution of potassium chloride or ammonium nitrate usually made rigid by boiling with agar agar and later cooling to a jelly like structure in the U tube). This provides an electric contact between the two solutions without allowing them to mix with each other. The zinc and copper rods are connected by a metallic wire with a provision for an ammeter and an on/off switch. The set up as shown in Fig.9.2 is known as **Daniell cell**. When the switch is in the off position, no reaction takes

place in either of the beakers and no current flows through the metallic wire. As soon as the switch is in the on position, we make the following observations :

1. Zinc rod starts dissolving and zinc sulphate solution becomes more concentrated.
2. Copper sulphate solution starts getting more diluted and metallic copper starts depositing. The over all reaction is,

   $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$.

   It may be noted that this is the same reaction that takes place when zinc rod is dipped in copper sulphate solution. In other words we have been able to separate the two half reactions by this arrangement when oxidation of zinc takes place in one beaker and reduction of copper ions takes place in the other beaker.
3. The transfer of electrons now does not take place directly from Zn to Cu^{2+} but through the metallic wire connecting the two rods as is apparent from the ammeter which indicates the flow of current. The electricity from solution in one beaker to solution in the other beaker flows by the migration of ions through the salt bridge. We know that the flow of current is possible only if there is potential difference between the copper and zinc rods.

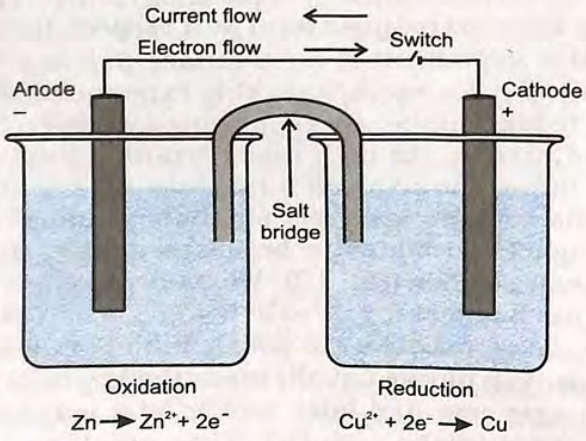


Fig.9.2 *The set up for Daniell cell. Electrons produced at the anode due to oxidation of Zn travel through the external circuit to the cathode where these reduce the copper ions. The circuit is completed inside the cell by the migration of ions through the salt bridge. It may be noted that the direction of current is opposite to the direction of electron flow.*

Student Activities

- Construct a Daniel cell and measure its e.m.f. by a voltmeter (of high internal resistance). Change the concentrations of zinc and copper ions and see the effect on the e.m.f. of the cell.
- Collect various types of batteries from your home and try to find out the redox reactions that lead to the production of electrical energy.

The difference of potential between the two electrodes is known by a special name called **electromotive force (e.m.f.)** We now have a voltaic or galvanic cell which is represented by

$Zn/Zn^{2+}(aq) \,||\, Cu^{2+}(aq)/Cu$

More information about the state of the electrodes and the concentration of the aqueous species can be given by representing the cell in the following manner:

$Zn(s)/Zn^{2+}(aq, 1\ M \,|\, KCl\ (saturated) \,|\, Cu^{2+}(aq, 1\ M/Cu(s)$

This gives us the information that Zn and Cu electrodes are in the solid form and the concentrations of copper and zinc ions are both equal to 1 M and the two half cells are connected by a salt bridge containing a saturated solution of potassium chloride. At each electrode interface there are two opposing reactions in which there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positive and the tendency of metal atoms to leave as ions into the solution and leave behind the electrons at the electrode.

At equilibrium there is a separation of charges and depending on the tendencies of the two opposing reactions the electrode may be positively or negatively charged with respect to the solution. Thus there exists an electric potential at both the electrodes and as soon as the switch is in the *on* position the electrons flow from negative electrode to less negative or positive electrode; or from less positive electrode to more positive electrode. The current flow is in the direction opposite to electron flow. **It is now an accepted convention that we keep the negative electrode on the left in the representation of the galvanic cell. Under this convention the e.m.f. of the cell is positive and is given by the potential of the half cell on the right hand**

side minus the potential of the half cell on the left hand side. It may be noted that each redox couple constitutes a half cell but we cannot measure the potential of individual half cell and can measure only the difference between the two half cells that gives the e.m.f. of the cell. However, the potential of each half cell depends on the activity (at lower concentrations it is equal to its molarity) of both the oxidized and the reduced forms of the species. Thus as the concentration of zinc ion increases and that of copper ion decreases, the e.m.f. of the cell decreases till it reaches zero when the potential of each electrode will be the same.

If we arbitrarily choose the potential of one electrode (half cell) then that of the other can be determined with respect to this. There is a convention that a half cell called **standard hydrogen electrode** (Fig.9.3) represented by – Pt, $H_2(g)/H^+(aq)$ – has zero potential at all temperatures. The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen is bubbled through it. The activity of both the reduced and oxidized forms of hydrogen is unity. This implies that the fugacity of hydrogen gas is one (nearly pressure of 1 bar) and the activity of hydrogen ion in the solution is one (nearly one molar HCl solution).

The e.m.f. at 298 K of the cell (standard hydrogen electrode direction || second half cell) constructed by taking **standard hydrogen electrode** on the left and the other half cell on the right gives the reduction potential of the other half cell. If the activities[2] of the oxidized and the reduced forms of the species in the right hand half cell are unity, then

$$E^0 = E^0_R - E^0_L = E^0_R - 0 = E^0_R$$

As E^0_L for standard hydrogen electrode is zero. The measured e.m.f. of the cell :

$Pt, H_2(g, 1\ bar)/H^+(aq, 1\ M) || Cu^{2+}(aq, 1\ M)/Cu$

is 0.34 V and is also the value for the standard reduction potential of the half cell corresponding to the reaction :

$Cu^{2+}(aq, 1M) + 2\ e^- \rightarrow Cu(s)$

Similarly, the measured e.m.f. of the cell :

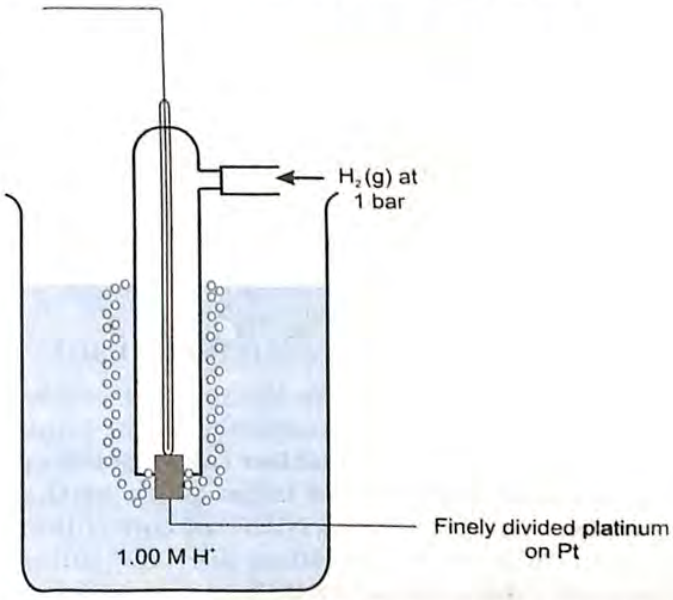


Fig.9.3 The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is partially dipped in an acidic solution (hydrogen ion molarity =1), through which hydrogen is bubbled at a pressure of =1 bar. The cell reaction is: $2H^+(aq, 1\ M) + 2e^- \rightleftharpoons H_2(g, 1\ bar)$ and arbitrarily choose that its $E^0 = 0$.

$Pt, H_2(g, 1\ bar)/H^+(aq, 1M) || Zn^{2+}(aq, 1M)/Zn$

is -0.76 V corresponding to the standard reduction potential of the half cell reaction:

$Zn^{2+}(aq, 1\ M) + 2e^- \rightarrow Zn(s)$

The positive value of the standard reduction potential in the first case indicates that hydrogen ion cannot oxidize Cu (or alternatively we can say that hydrogen gas can reduce copper ion) under the standard conditions described above. It may be mentioned that Cu does not dissolve in HCl. In nitric acid it is oxidized by nitrate ion and not by hydrogen ion. The negative value of the standard reduction potential in the second case indicates that hydrogen ion can oxidize (or zinc can reduce hydrogen ion).

2 *The activities of pure solids and liquids are taken as unity and in dilute aqueous solutions the activity of a given species is nearly equal to its molarity. For a gaseous species the activity is nearly equal to its partial pressure expressed in bar. Thus at 1 bar the activity of the gaseous species is nearly one.*

In view of this convention, the half reaction for the Daniell cell in Fig. 9.1 can be written as:

Left electrode : Zn^{2+} (aq, 1 M) + 2 e^- → Zn(s)

Right electrode: Cu^{2+} (aq, 1 M) + 2 e^- → Cu(s)

The overall reaction of the cell is the reduction reaction at the right hand side electrode minus the reduction reaction at the left hand side electrode and we obtain the equation:

$Zn(s) + Cu^{2+}(aq) = Zn^{2+}(aq) + Cu(s)$,

e.m.f. of the cell $= E^0 = E^0_R - E^0_L$

$= 0.34V - (-0.76)V = 1.10\ V$

It may be noted that the left hand electrode (anode) is negative with respect to right hand electrode (cathode). **Oxidation takes place at the anode and reduction takes place at the cathode.** According to international convention standard reduction potentials are now called **standard electrode potentials**.

The standard electrode potentials are very important and we can extract a lot of useful information from them. The values of standard electrode potentials for some selected half cell reduction reactions are given in Table 9.1. **If the standard electrode potential is greater than zero then its reduced form is more stable compared to hydrogen gas. Similarly if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of species.** It can be seen that the standard electrode potential for fluorine is the highest in the table indicating that fluorine gas is a very powerful oxidizing agent and fluoride ion is a very poor reducing agent. Lithium ion has the lowest electrode potential indicating that lithium ion is a very poor oxidizing agent while lithium metal is a very powerful reducing agent. It may be seen that as we go from top to bottom in Table 9.1 the standard electrode potential decreases and with this decrease the oxidizing power of the species on the left and increases the reducing power of the species on the right hand side of the reaction. Much more extensive table for standard reduction potentials are available in literature and are widely used in calculating equilibrium constants and other thermodynamic properties. Electrochemical cells are extensively used for determining the activity coefficients of electrolytes, pH of solutions, solubility product and for potentiometric titrations. On the basis of standard electrode potentials, we shall also examine the stability of inorganic and organic species in the Units to be covered later. We shall study electrochemical cells in greater detail in class XII. We shall illustrate the use of the standard reduction potential in redox reactions with the help of a few examples.

1. ***A negative E^o means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.***
2. ***A positive E^o means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.***

Example 9.12

The standard electrode potential corresponding to the reaction $Au^{3+}(aq) + 3e \rightarrow Au(s)$ is 1.42 V. Predict if gold can be dissolved in 1 MHCl solution and on passing hydrogen gas through gold salt solution, metallic gold will be precipitated or not.

Solution

The standard reduction potential is greater than zero therefore the reduced form of gold is more stable than hydrogen i.e. gold cannot be oxidized by hydrogen ion to give hydrogen. Hence gold does not dissolve in 1 M HCl solution. On the contrary if hydrogen gas is passed through the salt solution of the gold it will reduce auric ion and metallic gold will be precipitated.

In the same way we can determine the relative stability of various reduced species from the corresponding values of the standard reduction potentials involving these species. Thus for the reactions: $Ag^+(aq) + e^- \rightarrow Ag(s)$ and $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ the corresponding reduction potentials are 0.85 and – 0.76 V respectively. It is obvious that the reduced form (Ag) of the first reaction is more stable than the reduced form (Zn) of the second reaction. Hence silver will deposit if Zn metal is dipped in a silver salt solution.

Table 9.1 The standard electrode potentials at 298K

Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s respectively.

Reaction (Oxidized form + n e^-		Reduced form)	E° / V
Strongest oxidizing agent	$F_2(g) + 2\ e^-$	$\rightarrow 2F^-$	2.87
	$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
	$H_2O_2 + 2\ H^+ + 2\ e^-$	$\rightarrow 2H_2O$	1.78
	$MnO_2(s) + 4\ H^+ + 2\ e^-$	$\rightarrow Mn^{2+} + 2\ H_2O$	1.61
	$Au^{3+} + 3\ e^-$	$\rightarrow Au(s)$	1.50
	$MnO_4^- + 8\ H^+ + 5\ e^-$	$\rightarrow Mn^{2+} + 4\ H_2O$	1.49
	$Cl_2(g) + 2\ e^-$	$\rightarrow 2\ Cl^-$	1.36
	$Cr_2O_7^{2-} + 4\ H^+ + 6\ e^-$	$\rightarrow 2\ Cr^{3+} + 7\ H_2O$	1.33
	$O_2(g) + 4\ H^+ + 4\ e^-$	$\rightarrow 2\ H_2O$	1.23
	$Br_2(l) + 2\ e^-$	$\rightarrow 2\ Br^-$	1.09
	$NO_3^- + 4\ H^+ + 3\ e^-$	$\rightarrow NO(g) + 2\ H_2O$	0.97
	$2\ Hg^{2+} + 2\ e^-$	$\rightarrow Hg_2^{2+}$	0.92
	$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
	$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
	$O_2(g) + 2H^+ + 2\ e^-$	$\rightarrow H_2O_2$	0.68
	$I_2(s) + 2\ e^-$	$\rightarrow 2I^-$	0.54
	$Cu^+ + e$	$\rightarrow Cu(s)$	0.52
	$Cu^+ + 2\ e^-$	$\rightarrow Cu(s)$	0.34
	$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
	$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
	$2\ H^+ + 2\ e^-$	**$\rightarrow H_2(g)$**	**0.00**
	$Pb^{2+} + 2\ e^-$	$\rightarrow Pb(s)$	-0.13
	$Sn^{2+} + 2\ e^-$	$\rightarrow Sn(s)$	-0.16
	$Ni^{2+} + 2\ e^-$	$\rightarrow Ni(s)$	-0.25
	$Fe^{2+} + 2\ e^-$	$\rightarrow Fe(s)$	-0.44
	$Cr^{3+} + 3\ e^-$	$\rightarrow Cr(s)$	-0.74
	$Zn^{2+} + 2\ e^-$	$\rightarrow Zn(s)$	-0.76
	$Al^{3+} + 3\ e^-$	$\rightarrow Al(s)$	-1.66
	$Mg^{2+} + 2\ e^-$	$\rightarrow Mg(s)$	-2.36
	$Na^+ + e^-$	$\rightarrow Na(s)$	-2.71
Weakest oxidizing agent	$Ca^{2+} + 2\ e^-$	$\rightarrow Ca(s)$	-2.87
	$K^+ + e^-$	$\rightarrow K(s)$	-2.93
	$Li^+ + e^-$	$\rightarrow Li(s)$	-3.05

Increasing strength of oxidizing agent ↑

Weakest reducing agent

Increasing strength of reducing agent ↓

Strongest reducing agent

SUMMARY

Redox reactions form an important class of reactions in which *oxidation and reduction takes place simultaneously by transfer of electrons from the reductant to oxidant.* Thus the reductant (reducing agent) is oxidized by donating electrons to the oxidant (oxidizing agent) which in turn is reduced by accepting electrons. The concept of oxidation number is introduced in this Unit. It measures the extent of oxidation of an element in its given compound i.e. it gives the oxidation state of the element. A recipe is given for its assignment to each element in a compound. it was noted that if the oxidation number of an element in a compound increases that compound is oxidized and it acts as reducing agent. Similarly, if the oxidation number of an element in a compound decreases the compound is reduced and it acts as an oxidant. This helps us in identifying oxidizing and reducing agents in a reaction and also in balancing the chemical equation corresponding to that reaction. It has been shown that balancing of equation can also be done if we split the redox reaction into two half reactions corresponding to reduction and oxidation. The concept of *redox couple* is introduced leading to the construction of voltaic cell which can be used as a device for converting the energy of the redox reaction into electrical energy. The standard reduction potential is defined operationally with respect to standard hydrogen electrode. The oxidizing and reducing capacities of various species can be estimated from the standard reduction potential of the redox couple.

EXERCISES

9.1 Determine the oxidation number of the element in bold in the following species :
SiH_4, **B**H_3, **B**F_3, $\mathbf{S_2}O_3^{2-}$, **Br**O_4^- and HPO_4^{2-}.

9.2 Determine the oxidation number of C in the following:
C_2H_6, C_4H_{10}, CO, CO_2 and HCO_3^-.

9.3 Determine the oxidation number of O in the following:
OF_2, Na_2O_2 and CH_3COOH.

9.4 Identify the oxidants and reductants in the following reactions:
(a) $CH_4(g) + 4\ Cl_2(g) \rightarrow CCl_4(g) + 4\ HCl(g)$
(b) $2\ H^+(aq) + MnO_2(s) + C_2H_2O_4(aq) \rightarrow Mn^{2+}(aq) + 2CO_2(g) + 2\ H_2O(l)$
(c) $I_2(aq) + 2\ S_2O_3^-(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}$
(d) $Cl_2(g) + 2\ Br^-(aq) \rightarrow 2\ Cl^-(aq) + Br_2(aq)$

9.5 Balance the following equations in acidic medium by both oxidation number and ion electron methods and identify the oxidants and the reductants:
(a) $MnO_4^-(aq) + C_2H_2O_4(aq) \rightarrow Mn^{2+}(aq) + CO_2(g) + H_2O(l)$
(b) $H_2S(aq) + Cl_2(g) \rightarrow S(s) + Cl^-(aq)$
(c) $MnO_4^-(aq) + C_2H_5OH(aq) \rightarrow Mn^{2+}(aq) + CH_3COOH(aq)$
(d) $As_2S_3(s) + NO_3^-(aq) \rightarrow AsO_4^-(aq) + NO(g) + S(s)$

9.6 Balance the following equations in basic medium by both the oxidation number and ion electron methods and identify the reductants and the oxidants:
(a) $P(s) + OH^-(aq) \rightarrow PH_3(g) + H_2PO_2^-(aq)$
(b) $N_2H_4(g) + ClO_3^-(aq) \rightarrow NO(g) + Cl^-(g)$
(c) $Cl_2O_7(g) + H_2O_2(aq) \rightarrow ClO_2^-(aq) + O_2(g)$

9.7 Write the half reactions for the following redox reactions :
(a) $2\ Fe^{3+}(aq) + 2\ I^-(aq) \rightarrow 2\ Fe^{2+}(aq) + I_2(aq)$
(b) $Zn(s) + 2\ H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
(c) $Al(s) + 3\ Ag^+(aq) \rightarrow Al^{3+}(aq) + 3\ Ag(s)$

9.8 Calculate the standard e.m.f. of the cells formed by different combinations of the following half cells :
$Zn(s)/Zn^{2+}$ (aq), $Cu(s)/Cu^{2+}$(aq), $Ni(s)/Ni^{2+}$ (aq), and $Ag(s)/Ag^{+}$ (aq). (Consult Table 9.1)

9.9 With the help of table 9.1 select the oxidants which can oxidize (a) Cl^{-}(aq) to $Cl_2(g)$, (b) Fe (s) to Fe^{2+} (aq) and (c) I^{-}(aq) to I_2(aq).

9.10 With the help of table 9.1 select the reducing agent that can reduce the following ions to their metallic state :
Ag^{+} (aq), Al^{3+} (aq) and Ni^{2+} (aq)

9.11 Is it possible to store :
(i) Copper sulphate solution in a Zinc vessel?
(ii) Copper sulphate solution in a nickel vessel?
(iii) Copper sulphate solution in a silver vessel?
(iv) Copper sulphate solution in a gold vessel?

9.12 Determine the oxidation number of all the atoms in the following well known oxidants: $KMnO_4$, $K_2Cr_2O_7$, and $KClO_4$

9.13 Split the following redox reactions in the oxidation and reduction half reactions :
(a) $2K(s) + Cl_2(g) \rightarrow 2\ KCl(s)$
(b) $2\ Al(s) + 3\ Cu^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Cu(s)$

9.14 Identify the strongest and weakest reducing agents from the following metals :
Zn, Cu, Ag, Na, Sn (Consult Table 9.1)

9.15 Determine the change in the oxidation number of S in H_2S and SO_2 in the following industrial reaction :
$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(g)$

UNIT 10

PRINCIPLES AND PROCESSES OF EXTRACTION OF ELEMENTS

Objectives

After studying this Unit, you will be able to

- know the origin and cosmic abundance of elements, distribution and abundance in the earth's crust.
- understand the general principles and processes of extraction of elements.
- describe the process of extraction of metals in terms of concentration of ores, production of crude metals from concentrated ores, and refining of crude metals.

In the earlier classes we learnt that elements are the basic units of all types of matter. How were these elements initially formed? How are they distributed on earth? What are their modes of occurrence in the earth's crust and how are they obtained in pure form? We will address all these questions in this unit to seek plausible answers for them. Since about 80 per cent of the elements known are metals, their extraction/isolation/purification naturally form the major part of the study in this unit.

The initial formation of elements is related to various nuclear phenomena and their modes of occurrence in the earth's crust are governed by many factors. The naturally occurring chemical substances in the earth's crust which are obtained by mining are known as ***minerals.*** Minerals which can be used as a source for commercial recovery of a desired substance are termed as ***ores.*** Ores are usually associated with earthy materials called ***gangue.*** **Metallurgy** constitutes the scientific and technological process used for separating metals from their ores. **The three major steps in the extraction of a metal are: i) concentration of the ore, ii) isolation of the metal, and iii) purification of the metal.**

10.1 ORIGIN OF ELEMENTS

According to the current views, within two hours of the beginning of the universe there was a great fall in temperature. Most of the matter in the universe still consisted of hydrogen (89%) and helium (11%). The aggregate clouds of H and He atoms resulted in the formation of stars. The stars under the influence of gravity gave rise to high temperatures and densities within them. Vigorous nuclear events occurred as nuclei began to merge together. The energy released in nuclear fusion reactions led to the formation of elements up to iron, Fe (at.no. 26) constituted the stellar interior. The elements higher than Fe were produced by a variety of

nuclear processes such as the capture of neutrons produced from the lighter elements. For example

$^{23}_{10}Ne + ^{4}_{2}He \rightarrow ^{26}_{12}Mg + ^{1}_{0}n$

$^{98}_{42}Mo + ^{1}_{0}n \rightarrow ^{99}_{42}Mo + \gamma + \text{neutrino}$

$\rightarrow ^{99}_{43}Tc + \beta^-$

The daughter nuclide may capture more neutrons and may give rise to elements of higher atomic numbers.

Elements are also produced under the impact of cosmic radiations in the upper regions of atmosphere. For example, ^{14}C is produced in this way

$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}H$

This reaction still continues and is responsible for the steady concentration of ^{14}C in the living world.

Note : *In the nuclear reactions, the number on the top left of the symbol of the element denotes the mass number whereas the one at the bottom left represents the atomic number.*

10.2 DISTRIBUTION OF ELEMENTS ON EARTH

While considering the terrestrial distribution, it is useful to bear in mind the concept of volatility. Thus, an element may be volatile itself (like noble gases) or form compounds that are volatile under the conditions prevailing at the time of condensation of the earth. Other elements may be non-volatile. Some members of the two classes are:

Volatiles : C, halogens, Hg, Pb, Zn

Non-volatiles : Fe, Co, Ni, Si, Be, Ca

It is reasonable to believe that nonvolatile or less volatile elements may have their terrestrial distribution somewhat similar to the overall cosmic distribution. On the other hand the more volatile elements are greatly depleted on earth due to their loss during the high temperature periods accompanying the formation of earth.

Cosmic Abundances of Elements

The cosmic abundances of elements are shown in Fig.10.1. These are only approximate data as the elements are not uniformly distributed. The main problem is that there are concentrations of certain elements in different regions of the earth. Another problem is that the earth is not uniform from its core to its crust. Further, the composition of other planets are not the same as that of the earth. Often terrestrial abundances bear little relation to cosmic abundances.

Nevertheless, there is broad agreement that the information given here is considerably reasonable. Thus a number of conclusions can be drawn from this.

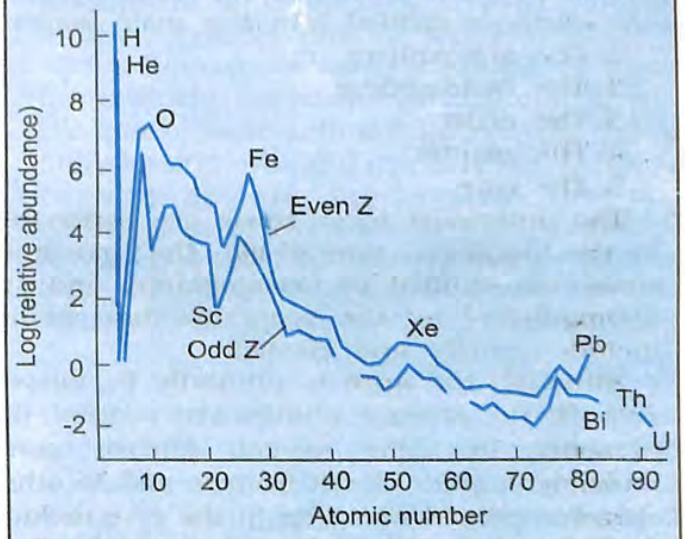


Fig.10.1 *Cosmic abundances of the elements. Elements with odd Z (atomic number)are less abundant than their neighbours with even Z. The abundances have reference to the number of atoms of each element relative to Si (taken as 10^6).*

For reasons related to the stabilities of nuclei, cosmic abundances alternate between elements of odd and even atomic numbers, with elements of even atomic numbers generally more dominant (Fig. 10.1). The high concentration of Fe is attributed to its very high nuclear binding energy. The low abundances of certain light elements such Li, Be and B are probably due to their ability to react with more of α-particles, thus

$^{8}_{4}Be + ^{4}_{2}He \rightarrow ^{12}_{6}C$

10.2.1 Condensation Processes

The early condensates appear in minerals that condensed at relatively high temperatures

and suffered little loss. A relatively depleted group consists of the moderately volatile elements which include Ag, Zn, Ge, Sn and F. A highly depleted group of volatile elements are Cd, Hg, Pb and the halogens other than F. The early condensates include metallic Fe (with 12.5 per cent Ni) *diopside* ($CaMgSi_2O_6$) and *anorthite* ($CaAl_2Si_2O_8$). Thus Fe, O, Mg and Si account for about 90 per cent of the earth and elements S, Ni, Al and Ca account for another 6 to 7 per cent.

10.2.2 Zonal Distribution

The earth is divided into five main zones.

1. The atmosphere
2. The hydrosphere
3. The crust
4. The mantle
5. The core

The outermost three zones are permeated by the biosphere, zone of life. The three inner zones are studied by seismography and are distinguished by the properties that mainly include density and elasticity.

Although the **core** is primarily Fe alloyed with Ni the seismic studies also suggest the presence of some oxygen and/or more probably sulphur. Apart from Fe and Ni other elements alloyed with iron in the core include Co, Pd and Rh. The elements present in the core are collectively known as *siderophiles* (from the Greek word *sideros* for iron).

The **lower mantle**, which is very dense, is probably dominated by $MSiO_3$ and MO minerals where M is Mg^{2+} and Fe^{2+}. A rich variety of aluminosilicate minerals dominate the earth from the upper mantle to the crust. In the *Goldschmidt classification*, the elements that concentrate in these structures are known as *lithophiles* (from the Greek word *lithos* for stone). They include Na, K and Ca and cations of the later *d*-block and *p*-block elements. Out of these Cu, Zn, As and Pb are commonly found as sulphides. These are called *chalcophiles* (from the Greek word *khalkos* for copper and brass).

The outer fluid zones – the hydrosphere of ocean and atmosphere – jointly concentrate the small molecular species which include O, N and Ar. These elements are known as *atmophiles* (from the Greek word *atmos*, vapour). These zones and their probable composition are shown in Fig.10.2.

An element may be prominent in more than one geochemical category. For example oxygen is important both as a lithophile and an atmophile.

10.3 ABUNDANCES OF ELEMENTS IN THE EARTH'S CRUST

Clues to the interior of the earth crust come mainly from boreholes. Light elements such as oxygen, silicon and aluminium make up the earth's crust. Oceanic crust is mostly basalt (which also contains magnesium and iron). Continental crust is composed of two main types of igneous rocks:

(i) Light rocks, i.e. granite and related types (containing 70 per cent SiO_2 together with Al_2O_3).

(ii) Heavy rocks i.e. basalt (containing 40–50 per cent SiO_2 together with MgO).

Aluminium is the second most abundant element in the light rocks and magnesium is the second most abundant element in the heavy rocks.

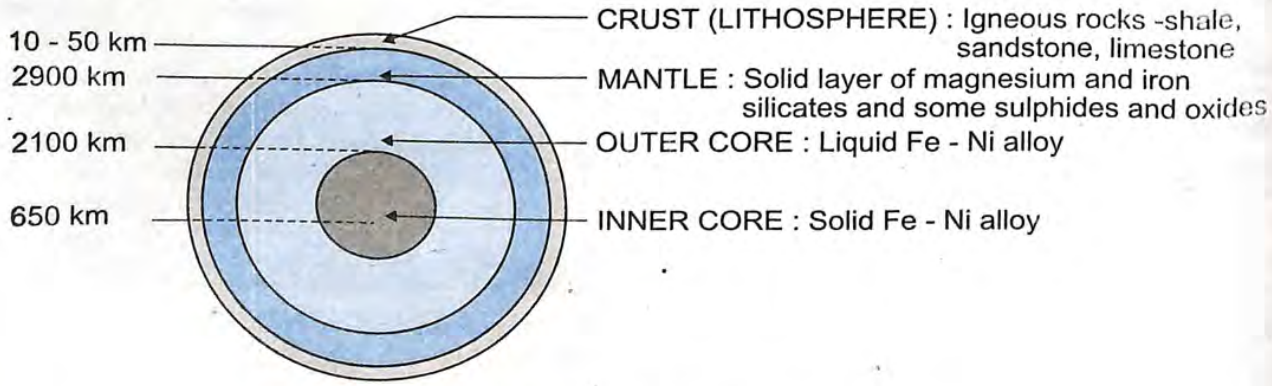

10 - 50 km
2900 km
2100 km
650 km
CRUST (LITHOSPHERE) : Igneous rocks -shale, sandstone, limestone
MANTLE : Solid layer of magnesium and iron silicates and some sulphides and oxides
OUTER CORE : Liquid Fe - Ni alloy
INNER CORE : Solid Fe - Ni alloy

Fig.10.2 Main zones in the earth's interior

Convection currents both in the air above and in the molten mass below the crust probably caused a continual break up and rebuilding of the crust giving rise to high (continent) and low (ocean) regions. The earth's crust also suffered erosion by water, air and carbon dioxide producing sedimentary materials (clay, sand and mud) which deposited in rivers, lakes and oceans. Continued deposition of sedimentary materials resulted in the formation of sedimentary rocks such as limestone, chalk and sandstone which constitute about 5 per cent of the earth's crust. These sedimentary rocks provide the most readily available source of ores.

Over 100 elements are known at the present time. Eighty-eight have been found in nature and the remaining have been synthesized. Oxygen constitutes nearly half and silicon one-quarter of the total mass of elements in the earth's crust. The sixteen most abundant elements in the earth's crust and their percentages by weight are listed in Table 10.1.

Two points may be recalled here: (1) elements with low atomic numbers constitute a major portion of the earth's crust and (2) elements with even atomic numbers are generally more abundant than elements with odd atomic numbers. There are some exceptions to (2). The noble gases (with even atomic numbers) occur only to a minute extent as these probably escaped in the atmosphere during the condensation period.

Example 10.1

Give examples of igneous and sedimentary rocks: What is the origin of igneous rocks and what is the origin of sedimentary rocks?

Solution

Igneous rock : granite.
Sedimentary rocks : chalk, sandstone, limestone.

Origin – Solidified matter from magma on cooling formed igneous rocks.
Sediments brought by rain or wind and deposited in rivers and lakes form sedimentary rocks.

10.4 ELEMENTS IN BIOLOGICAL WORLD

Many elements are accumulated in living organisms. Some of the familiar examples are: enrichment of iodine in sea weeds, vanadium in sea cucumber and Fe, Mg, K in plant life. Apart from the above, presence of iron in haemoglobin, magnesium in chlorophyll, zinc in the eyes of some animals, the enzyme carbonic anhydrase in cells and traces of Mn, Cu and Fe in chloroplasts are among the other occurrences of elements in living organisms. However, biological occurrences of elements (except for a few like iodine) rarely serve as a source for their isolation in elemental state.

10.5 OCEAN AS A SOURCE OF ELEMENTS

Oceans are rich source of many useful substances. Sea water, for example, contains nutrients and minerals. Oil and natural gas occur in continental shelf sediments. Metals such as gold and manganese are found in sediments on the ocean floor. Sea water receives many of the dissolved salts by way of weathering of the earth surface by rain water. This can be depicted by the following example:

Igneous rock + Rain water → Stream of water + Detritus clay (Clay + SiO_2)

$CaAl_2Si_2O_8$ ($H_2O + CO_2$) (Ca^{2+}, K^+, Na^+ + HCO^-_3)
(Ca - aluminosilicate)

$KA1.Si_3O_8$ (K - aluminosilicate),
$NaA1Si_3O_8$ (Na-aluminosilicate),

Table 10.1 Sixteen Most Abundant Elements in the Earth's Crust

Atomic Number	Element	Percentage (by weight)	Atomic Number	Element	Percentage (by weight)
8	Oxygen	49.5	1	Hydrogen	0.9
14	Silicon	25.7	22	Titanium	0.6
13	Aluminium	7.5	17	Chlorine	0.2
26	Iron	4.7	15	Phosphorus	0.1
20	Calcium	3.4	25	Manganese	0.09
11	Sodium	2.6	6	Carbon	0.08
19	Potassium	2.4	16	Sulphur	0.06
12	Magnesium	1.9	56	Barium	0.04

(Total percentage weight of these elements = 99.77)

Marine organisms convert the Ca^{2+} ions into $CaCO_3$ (shells) which form sediments. Hydrochloric acid ejected by undersea volcanoes reacts with HCO^-_3 to form chlorides of Na, K and Ca in sea water. The relative abundance of elements in sea water is shown in Fig.10.3. It is interesting to note that a few elements, like chlorine, bromine, sodium and magnesium are recovered from sea water. Also some rare metals are recovered from manganese nodules which are occasionally found in sea bed.

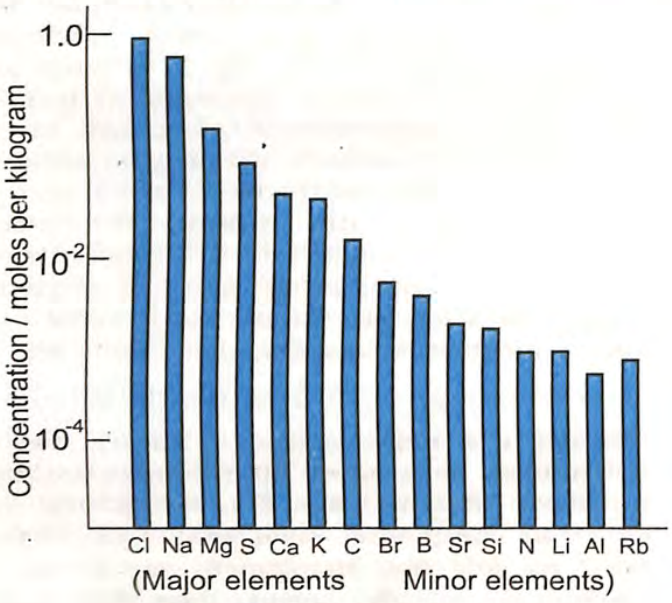


Fig.10.3 *Elements in sea*

Vast quantities of metallic salts are also held in solution in the oceans, the principal ions being Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, F^-, Cl^-, Br^-. In future sea water may become an important source of many metals such as uranium and gold.

10.6 MODES OF OCCURRENCE OF METALS

Elements may occur either in the free state or in the combined state. In the combined state the non-metals are found usually in the reduced form and the metals in the oxidised form. Most metals, except the very unreactive ones such as gold and platinum, occur in the combined form as minerals. The minerals are naturally occurring chemical substances in the earth's crust and are obtained by mining. The minerals are usually associated with earthy materials (gangue). Ores are the naturally occurring minerals from which metals can be profitably extracted. Metallic compounds found in the earth's crust usually have low solubility in water. The more soluble, naturally occurring compounds are found in sea water or in the large salt bed deposits formed by the evaporation of inland seas. Some important types of ores are listed in Table 10.2.

It may be noticed that often a metal occurs in more than one form and, therefore, the type of ore for a metal must not be interpreted too rigidly. It is important to realize, however, that in extracting elements from a mineral, the profitability angle is very important. Silicate minerals, for example, are

Table 10.2 Important Types of Ores

Ore type	Examples
Native	Cu, Ag, Au, Hg, As, Bi, Sb, Pd, Pt
Oxides	Al_2O_3, Fe_2O_3, Fe_3O_4, SnO_2, MnO_2, TiO_2, $FeCr_2O_4$, WO_3, Cu_2O, ZnO.
Carbonates	$CaCO_3$, $CaCO_3.MgCO_3$, $FeCO_3$, $PbCO_3$, $BaCO_3$, $SrCO_3$, $ZnCO_3$, $MnCO_3$, $CuCO_3.Cu(OH)_2$.
Sulphides	Ag_2S, Cu_2S, PbS, ZnS, HgS, FeS, Bi_2S_3, NiS, CaS, MoS_2.
Halides	NaCl, KCl, AgCl, $MgCl_2.6H_2O$; NaCl and $MgCl_2$ (in sea water)
Sulphates	$BaSO_4$, $SrSO_4$, $PbSO_4$, $CaSO_4.2H_2O$, $CuSO_4.2Cu(OH)_2$.
Silicates	$Be_3Al_2Si_6O_{18}$, Zn_2SiO_4, $Sc_2Si_2O_7$, $NiSiO_3$, $MgSiO_3$.
Phosphates	$CePO_4$, $LaPO_4$, $Th_3(PO_4)_4$, $LiF.AlPO_4$

not worked at present because of the difficulties attending the extraction of the elements from these minerals. Ores of low concentrations are worked only if they can be processed easily and economically. The required minimum concentration varies from metal to metal. For example, for iron and aluminium it should be 30% or more but for copper it may be 1% or even less.

10.7 MINERALS FOUND IN INDIA

India is quite rich in a variety of minerals. Orissa and Bihar have the largest deposits of ores of iron, manganese, chromium in addition to coal, mica and phosphates. Madhya Pradesh, Maharashtra have sizeable reserves of manganese, chromium, bauxite and many other minerals. Rajasthan is rich in non-ferrous metals like copper, zinc and lead. Tamil Nadu has sizeable reserves of iron, manganese, mica, limestone and lignite. There are many industries producing iron, aluminium, zinc, gold, etc. The Steel Authority of India Limited (SAIL) is producing over 10 million tones of steel through its different steel plants. Table 10.3 gives principal minerals and their estimated reserves found in India.

Example 10.2

In general which metals do you expecpt to occur in the native state in nature? Give examples.

Solution

Those below hydrogen in the electrochemical series, e.g. Cu, Ag, Au, Pt, etc.

10.8 EXTRACTION OF ELEMENTS

As we have seen, not many elements occur in the free state in nature. In the combined states, metals are usually found in the oxidized form (e.g. Fe_2O_3, MnO_2, SnO_2) while non–metals are present in the reduced form such as X^- (X^- = Cl^-, Br^-, I^-). The methods of extraction or isolation of metals and non–metals from the natural sources are, therefore, quite different. Metals have to be freed from their oxidized forms by reduction while non -metals are obtained by oxidation. Their extractions are accordingly treated separately here. The reduction is brought about by electronation, i.e. by providing electron directly or indirectly while oxidation is carried out by de-electronation i.e. by removing electron, directly or indirectly.

Table 10.3 Chief Ores of Some Metals

Metal	Name of the Chief Ore	Estimated Reserves in India
Aluminium	Bauxite, $Al_2O_3.xH_2O$ Diaspore, $Al_2O_3.H_2O$	2460 million tonnes Orissa, Andhra pradesh, Madhya Pradesh, Bihar.
Chromium	Chromite, $Fe^{II}Cr^{III}_2O_4$ (or chrome iron stone)	86 million tonnes Orissa, Karnataka, Bihar, Maharastra.
Copper	Copper pyrites, $CuFeS_2$ Malachite, $Cu_2CO_3(OH)_2$	416 million tonnes Rajasthan, Gujarat.
Iron	Haematite, Fe_2O_3 Magnetite, Fe_3O_4	14000 million tonnes Madhya Pradesh, Bihar, Orissa, Karnataka.
Manganese	Pyrolusite, MnO_2	167 million tonnes Orissa, Madhya Pradesh, Karnataka, Goa.
Tin	Cassiterite, SnO_2 (or tin stone)	23000 tonnes Rajasthan, Andhra Pradesh.
Zinc	Zinc blende, ZnS; Calamine, $ZnCO_3$	179 million tonnes Rajasthan, Gujarat, Maharashtra.
Lead	Galena, PbS	

10.8.1 Extraction of Non-metallic Elements

Non-metallic elements occurring in the combined form are generally extracted by oxidation. Among such elements the halogens are the most important ones. Consider, for example, the oxidation of Cl^- ions in water:

$$2Cl^-(aq) + 2H_2O(l) \rightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$$

The oxidation of Cl^- ions to chlorine cannot be brought about by ordinary chemical methods. The oxidation of Cl^- is accomplished by electrolysis. The minimum potential difference required for this is 2.2V. Similarly fluorine is also extracted by electrolysis. Elements like oxygen, nitrogen and noble gases are available from air. Carbon, sulphur and phosphorus are extracted either from native ores or by oxidation from their compounds occurring in nature. Since there are no general methods of extraction of non-metals, individual cases will be considered while dealing with the chemistry of individual elements at the appropriate places in the text (Unit 13).

10.8.2 Extraction of Metals : Metallurgy

Except for the most unreactive ones, metals are extracted from their ores by reduction processes. But before an ore is subjected to reduction, it has to be subjected to various operations such as concentration, roasting, smelting, etc. The whole process of extraction of a metal in pure form from its ore is known as *metallurgy* (Fig.10.4).

The three main stages of metallurgy are:

(1) Concentration of ore.
(2) Extraction of crude metal from the concentrated ore.
(3) The refining of the crude metal.

Different methods are available for each of these stages. The choice of the method employed, in a particular case, depends on factors such as the type of impurity, the type of metal, available facility, etc. All these points are discussed in detail with suitable examples in the following paragraphs.

The 1600 year old **Delhi iron pillar** in the vicinity of Kutab Minar is testimony to high level skill in metallurgy achieved by the Indians.It has attracted the attention of metallurgists and corrosion scientists for its excellent resistance to corrosion. It is essentially made of wrought iron 99.72%, carbon 0.08%, silicon 0.046%, sulphur 0.006%, phosphorus 0.114% and manganese nil. Since 400 A.D. it has been existing without any rust or sign of decay. This may be due to formation of a thin film of magnetic oxide (Fe_3O_4) on the surface as a result of finishing treatment given to the pillar, such as painting with a mixture of different salts, heating and quenching.

Fig.10.3(a) Iron Pillar at Delhi

10.8.2(a) Concentration of the Ore

The process of removal of the unwanted material (gangue) from the ore is called ***concentration***, ***dressing*** or ***benefaction*** of the ore. The ore is graded, pulverized, and ground to a powder in the crushers and grinders. It is then concentrated to remove the gangue. The important methods for concentration are:

(i) Hydraulic washing : The method is based on the difference in specific gravities of the ore and gangue particles. It is also known as *gravity separation method.* In one of the adaptations, the powdered ore is washed with an upward stream of running water when the lighter gangue particles are washed away while the heavier ore particles (concentrated form) are left behind

(ii) Magnetic separation : The method is based on magnetic and non magnetic properties of the two components of the ore

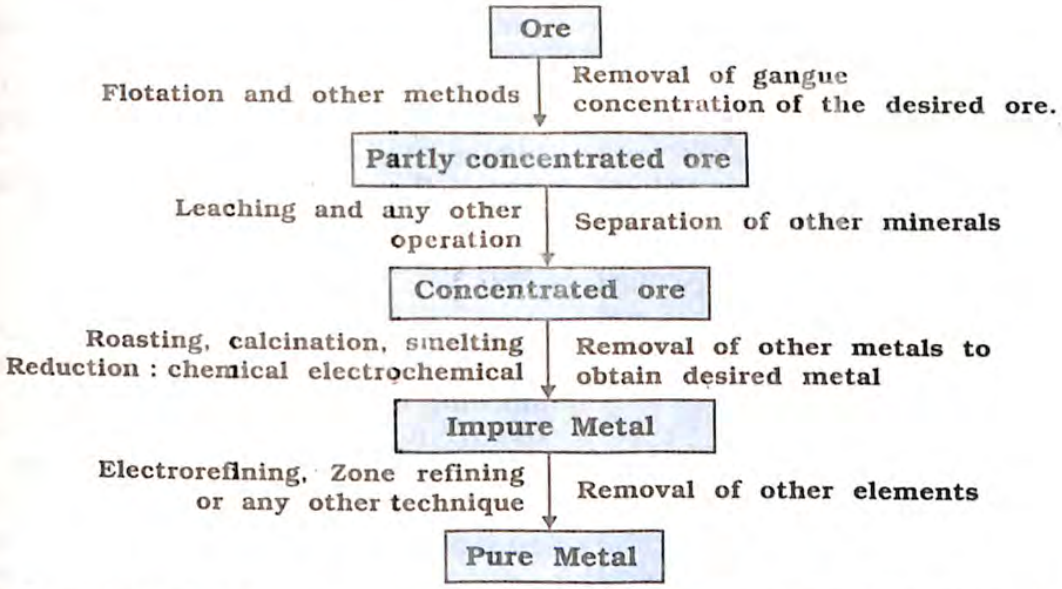

Ore
Flotation and other methods
Removal of gangue concentration of the desired ore.
Partly concentrated ore
Leaching and any other operation
Separation of other minerals
Concentrated ore
Roasting, calcination, smelting
Reduction : chemical electrochemical
Removal of other metals to obtain desired metal
Impure Metal
Electrorefining, Zone refining or any other technique
Removal of other elements
Pure Metal

Fig.10.4 *Flow sheet for general metallurgical operations [In the above flow sheet, the functions of processes are given on the right side, whereas the methods employed are denoted on the left]*

(pure, impure). This method, though cheap, has limited application. The ground ore is carried on a travelling band which passes over a magnetic roller (Fig. 10.5). The ore leaves the band and falls from it. The particles attracted by the magnetic field form a separated pile. The method is useful for separating tungsten ore particles from cassiterite (SnO_2). The process may also be employed for separating other transition metal ores, such as magnetite (Fe_3O_4), chromite (FeO, Cr_2O_3) and pyrolusite (MnO_2) from unwanted gangue.

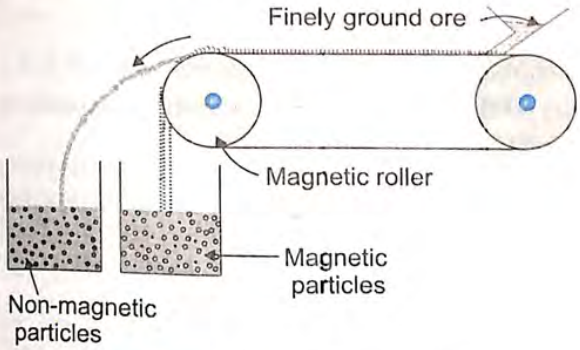


Fig.10.5 *Magnetic separation*

(iii) Froth flotation method: This is a very useful technique especially for separating sulphide ores of zinc, copper and lead from the gangue. A suspension of the finely powdered ore is made with water. To the suspension are added: *collectors* (e.g. pine oils, xanthates, and fatty acids) which enhance the nonwettability of the mineral particles, and *froth stabilizers* (e.g. cresols and aniline) which stabilize the froth.

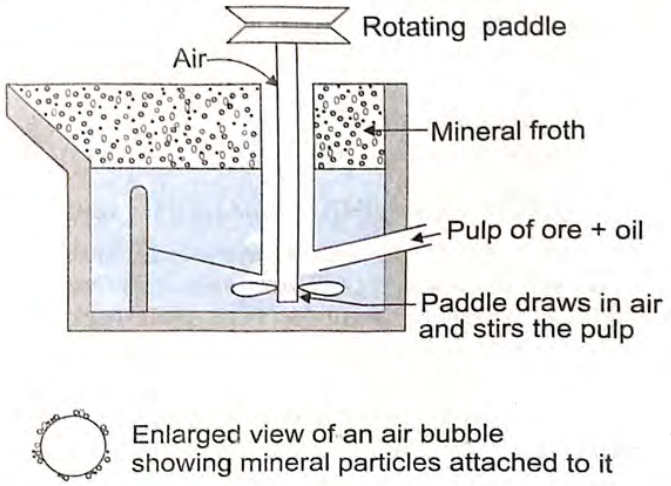

Rotating paddle
Air
Mineral froth
Pulp of ore + oil
Paddle draws in air and stirs the pulp
Enlarged view of an air bubble showing mineral particles attached to it

Fig.10.6 *Froth flotation method*

The principle of the process is that the mineral particles are wetted by oils and the gangue particles by water. A rotating paddle agitates the liquid mixture and draws in air causing the formation of a froth which carries with it the mineral particles. The light froth floats to the surface and is skimmed off. It is allowed to collapse and dry for recovery of

mineral particles. By adjusting the proportion of oil to water it is often possible to separate one sulphide ore from another.

Sometimes ***depressants*** are used to prevent certain type of particles from forming the froth with the bubbles. For example, sodium cyanide can be used as a depressant in the separation of zinc sulphide ore (ZnS) and lead sulphide ore (PbS). Sodium cyanide acts as a depressant for ZnS but does not prevent PbS from the formation of the froth. The two ores can thus be separated (see Fig.10.6).

Example 10.3

How does NaCN act as a depressant in preventing ZnS from forming the froth?

Solution

NaCN forms a layer of zinc complex, $Na_2Zn(CN)_4$ on the surface of ZnS and thereby prevents it from the formation of froth.

(iv) *Leaching*: This method is useful in case the ore is soluble in a suitable solvent. Some important examples are described below:

In the **Bayer's process** pure aluminium oxide is obtained from the bauxite ore by treating the powdered ore with a concentrated solution of sodium hydroxide when Al_2O_3 dissolves leaving behind the impurities:

$$Al_2O_3(s) + 2OH^-(aq) + 3H_2O \rightarrow 2Al(OH)^-_4(aq)$$

The solution of sodium aluminate is filtered and cooled and its pH is adjusted downward by dilution and/or neutralization with carbon dioxide when aluminium hydroxide is precipitated; seeding with a little freshly precipitated aluminium hydroxide quickens the process.

$$Al(OH)^-_4(aq) \xrightarrow[CO_2]{\text{dilution}} Al(OH)_3(s) + OH^-(aq)$$

The precipitate of $Al(OH)_3$ is filtered, dried and finally heated to about 1473K to obtain pure Al_2O_3.

$$2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(g)$$

The leaching method is also employed in concentrating silver and gold ores. The ore containing native metal is treated with a dilute solution of NaCN or KCN in the presence of air to obtain the metal in solution as a complex. Thus:

$$4M + 8CN^- + 2H_2O + O_2 \rightarrow 4M(CN)^-_2 + 4OH^-$$
(air) (soluble complex)

(where M = Ag or Au)

and if the ore happens to be sulphide (e.g. Ag_2S – argentite) it may react as:

$$Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$$
(soluble complex)

After concentrating the ore by any of the above methods, except (iv), the ore is set for smelting but being too fine it would either be blown out or choke up the furnace. The ore is, therefore, made into course lumps by the sintering process.

10.8.2(b) Extraction of the Crude Metal from the Concentrated Ore

The concentrated ore must be converted into a form which is suitable for reduction to the metal. If the ore is a hydroxide (hydrated oxide), carbonate or sulphide it is subjected to ***calcination*** or ***roasting / smelting*** and thereby converted to the oxide form. For thermodynamic reasons it is easier to reduce an oxide than the sulphide. (*see Example 10.4*)

Calcination : In this process the concentrated ore is heated in a regular supply of air when the volatile matter is burnt away and the oxide of the metal is obtained. Some examples are given below:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

$$Al_2O_3.2H_2O \rightarrow Al_2O_3 + 2H_2O$$

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaCO_3.MgCO_3 \rightarrow CaO + MgO + 2CO_2$$

A *reverberatory furnance* is usually employed for carrying out calcinations.

Roasting : In this process the ore (usually the sulphide) is heated in a regular supply of air at a temperature below the melting point of the metal. The metal is converted to the oxide or sulphate.

Sometimes a part of the sulphide may act as a reducing agent in the subsequent step. Some examples of roasting of ores are:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

$$PbS + 2O_2 \rightarrow PbSO_4$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

The process of roasting is generally carried out in a reverberatory furnace (Fig.10.7).

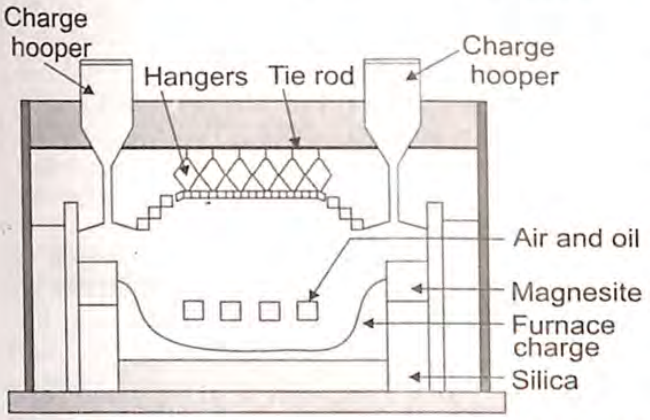


Fig.10.7 Section of a modern reverberatory furnace

Examples 10.4

Why is it advantageous to roast a sulphide ore to the oxide before reduction?

Solution

The free energies of formation (which you will study in class XII) ($\Delta_f G^\ominus$) of most sulphides are greater than those for CS_2 and H_2S. Carbon disulphide is in fact, an endothermic compound. So neither carbon nor hydrogen is a suitable reducing agent for metal sulphides. Moreover the roasting of a sulphide to the oxide is quite advantageous thermodynamically. Hence, the common practice is to roast sulphide ore to the oxide prior to reduction.

10.8.2(c) Reduction of the Roasted/Calcinated Ore to the Metallic Form

In general most of the metals which occur in the combined state are present in their positive oxidation states. They must therefore be reduced by electronation, providing electrons to become free metals. The nature of reducing agent to be used in a particular case depends on how difficult the reduction process is. If the metal is very reactive like the alkali metals, they can be reduced only by electrolytic method. Less reactive metals like copper, lead, tin, etc. can be reduced by chemical reducing agents. The choice of reducing agent is decided by the factors of energetics and economics.

Various reduction process are described under the four main categories, viz.

(a) Chemical reduction
(b) Auto reduction
(c) Displacement method
(d) Electrolytic reduction

(a) Chemical Reduction

(i) Carbon as a reducing agent **:** Carbon (in the form of coal, coke, charcoal and carbon monoxide) reduces many metal oxides into the respective metals. Some examples are:

$$SnO_2 + 2C \xrightarrow{1473\text{-}1573K} Sn + 2CO$$

(cassiterite)

$$ZnO + CO \xrightarrow{1600K} Zn + CO_2$$

$$Fe_2O_3 + CO \xrightarrow{823K} 2FeO + CO_2$$

$$FeO + CO \xrightarrow{1123K} Fe + CO_2$$

Production of Iron from the Oxide Ore

The extraction of iron, the most important industrial metal, is carried out in a blast furnace (Fig.10.8). The charge consists of iron ores (haematite, Fe_2O_3 and magnetite, Fe_3O_4), coke and limestone which is heated with a blast of air (Fig.10.8). As the exothermic reaction proceeds a composition and temperature gradient is set up in the furnance. Below 1123K, CO reduces the ores to FeO. Reduction to Fe by CO can occur at about 1123K and that direct reduction, in which the reducing agent is C can occur above 1123K. In this region limestone also decomposes to CaO and CO_2 and slag formation takes place.

[**Note:** Apart from the integrated steel plants which produce steel out of the pig iron from blast furnaces, steel is also produced by electronic arc furnaces and induction furnace units using steel scrap, sponge iron as feed material. While integrated steel plants produce mainly mild steel in bulk quantities, the electronic steel making units produce mild steel as well as alloy steel including stainless steel.]

(ii) Hydrogen as a reducing agent: Because of its inflammable nature it is used in very few cases e.g.

$MO_3 + 3H_2 \rightarrow M + 3H_2O$ (where M = Mo or W)

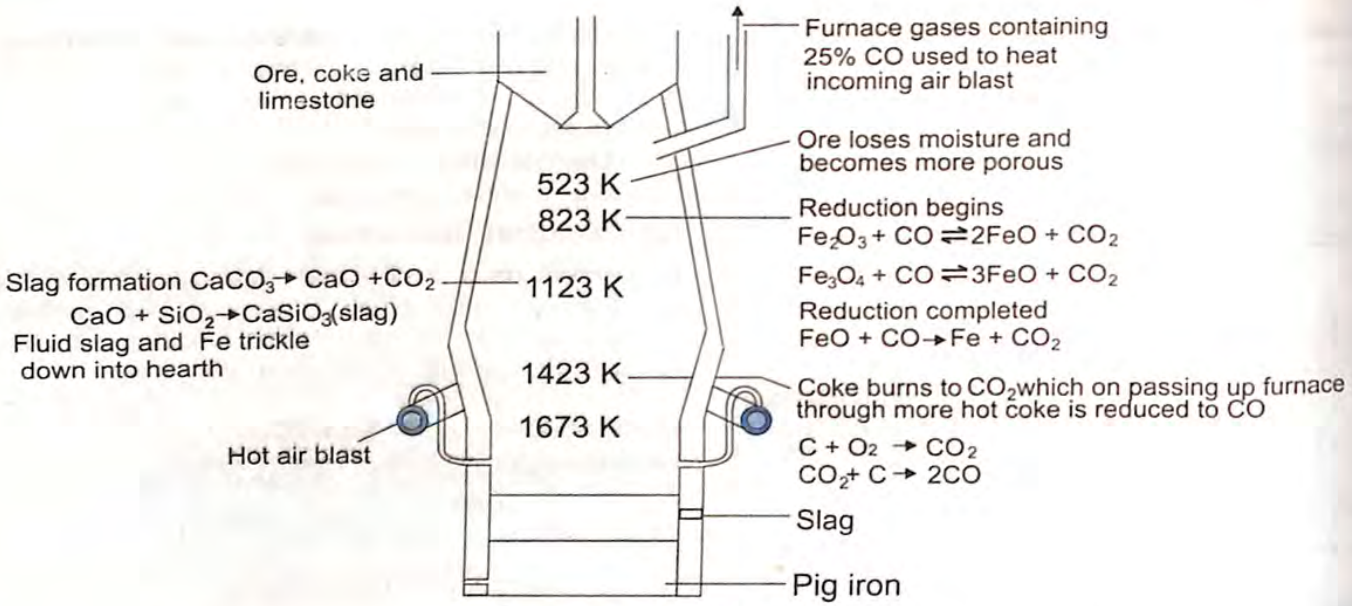

Furnace gases containing 25% CO used to heat incoming air blast
Ore, coke and limestone
Ore loses moisture and becomes more porous
523 K
823 K
Reduction begins
$Fe_2O_3 + CO \rightleftharpoons 2FeO + CO_2$
$Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2$
Reduction completed
$FeO + CO \rightarrow Fe + CO_2$
Slag formation $CaCO_3 \rightarrow CaO + CO_2$
$CaO + SiO_2 \rightarrow CaSiO_3$(slag)
Fluid slag and Fe trickle down into hearth
1123 K
1423 K
Coke burns to CO_2 which on passing up furnace through more hot coke is reduced to CO
1673 K
$C + O_2 \rightarrow CO_2$
$CO_2 + C \rightarrow 2CO$
Hot air blast
Slag
Pig iron

Fig.10.8 Blast furnance

(iii) Aluminium as a reducing agent : The oxides of chromium and manganese are reduced by aluminothermic reduction process/or Goldschmidt thermic process.

$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$

$3Mn_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Mn$

(iv) Other metals as reducing agents : Sodium and magnesium metals are used in certain cases such as titanium oxide TiO_2. Thus

$TiO_2 + 2Mg \rightarrow Ti + 2MgO$

or $TiO_2 + 4Na \rightarrow Ti + 2Na_2O$

(b) Auto-reduction

In certain cases no reducing agent is required. The metal is obtained either by simple roasting or by the reduction of its partly oxidized form. Thus, mercury is directly obtained by roasting its ore cinnabar (HgS) in air.

$HgS(s) + O_2(g) \rightarrow Hg(g) + SO_2(g)$ or

$2HgS(s) + 3O_2(g) \rightarrow 2HgO + 2SO_2$

$2HgO(s) \rightarrow Hg(g) + O_2$ also

$2HgO(s) + HgS(s) \rightarrow 3Hg(g) + SO_2(g)$

Cu_2S is also reduced by partly converted Cu_2O in this way during smelting. Similar is the case with PbS

$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$ and

$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2$

All roasting/smelting processes mentioned above make use of reverberatory furnaces at some stage. The diagram of such a modern furnace is shown in Fig.10.7. Oil burners shoot along intensely hot flame down the furnace and melt the charges. On the walls there are suitable tap holes for crude metals and the slag. Such a furnace may melt upto 10^6kg of charge per day. Smelting operations can also be carried out in converters. Air is blown through the molten material, when the impurities are largely removed as volatile oxidation products. Also magnesite linings are used in converters to slag off any metallic impurities. Converters may be of two types: ***(1) Bessemer converter***, similar to that used in metallurgy of iron. ***(2) The Pierce-Smith converter*** which consists of a large horizontal steel drum resting upon rollers. Rolls of steel tubes (tuyeres) pass into the converter and are connected to an air duct. Air is forced into the molten bath of crude metal. The process provides its own heat due to the oxidation of impurities and the temperature rises to ~ 2673K.

(c) Displacement Method

Some metals are reduced by displacement by a more reactive metal, from their complexes. Silver and gold, for example, are obtained from their complex cyanides when more reactive zinc metal displaces them:

$2M(CN)_2^- + Zn \rightarrow Zn(CN)_4^{2-} + 2M$

(where M = Ag or Au)

Electrolytic reduction and cell potential: The electrolytic reduction can be regarded as a technique for driving a reduction by coupling it through electrodes and external circuitry. We know (see Unit 9) that reduction takes place at one electrode and oxidation takes place at the second. By applying external potential from an outside source, reduction is brought at the desired electrode.

(d) Electrolytic Reduction

Highly electropositive elements of groups 1 and 2 are reduced by electrolytic method. These metals which occur as chlorides or oxosalts are converted into their chlorides. When electric current is passed through a fused chloride, the M^{n+} ions are discharged at negative electrode (cathode) and deposited. In the electrolysis of brine (NaCl) using Hg cathodes, Na^+ is discharged at cathode and forms an amalgam. This takes place in preference to the liberation of H_2 (expected from electrochemical series) due to high H_2 overvoltage at Hg cathode

$$\text{Na} \xleftarrow[\text{(at cathode)}]{\overset{\text{discharged}}{e^+}} \text{Na}^+ \leftarrow \boxed{\begin{matrix}\text{NaCl}\\ \text{brine}\end{matrix}} \rightarrow \text{Cl}^- \xrightarrow[\text{(at anode)}]{\overset{\text{discharged}}{-e^-}} \tfrac{1}{2}\text{Cl}_2$$

Metals other than the s - block can also be extracted by electrolysis of fused compounds, e.g., fused Al_2O_3 mixed with Na_3AlCl_6 is used for the production of Al. It may be noted here that the general scheme of extracting metals as outlined above is altered in special cases. Sometimes more steps than mentioned above may be necessary, whilst at times fewer steps may serve the purpose. These steps will be discussed while dealing with the individual cases at the appropriate places in the text.

10.8.2(d) Refining of Crude Metals

Metals extracted by any of the methods described above are usually contaminated with some impurity. Various methods of refining are employed depending upon the nature of metal and the nature of impurity. Some of these methods are briefly outlined below.

(i) Distillation : This is useful for low boiling metals. Examples are purification of zinc and mercury.

(ii) Liquation : A low melting metal like tin can be made to flow on a sloping surface and thus separated from higher melting impurities.

(iii) Electrolysis : This method is widely used in the refining of copper, gold, silver, lead, zinc, aluminium etc. The impure metal is made the anode and a pure strip of the same metal the cathode in a suitable electrolytic bath. The process takes place as:

Anode : $M \rightarrow M^{n+} + ne^-$

Cathode: $M^{n+} + ne^- \rightarrow M$

The net result is the transfer of pure metal from the anode to the cathode. The applied voltage is such that more electropositive metals (impurity) remain as ions in the bath whereas the less electropositive metals (impurities) remain unionized and fall down as anode mud. Thus in the electrolytic refining of copper more basic metals like zinc remain in the solution as cations, whereas less basic ones like, Te, Ag, Au, etc. go to the anode mud.

(iv) Zone refining : This method is employed to get metals of very high purity. Germanium, silicon, boron, gallium, indium are purified by this method. The method is based on the principle that the impurities are more soluble in the melt than in the pure metal. A circular mobile heater is fixed at one end of a rod of the impure metal. The heater is slowly moved forward. The melted zone moves along with the heater. As the heater moves forward the pure metal crystallizes out of the melt while the impurities pass into the adjacent molten zone. The process is repeated a number of times until the desired state of purity is reached. The end of the rod where the impurities finally get concentrated is cut off. The method is specially useful for producing semiconductors of very high purity. Germanium, for example, purified by this method contains as little as 10–7 ppm of the impurities (Fig. 10.9).

(v) Vapour phase refining : This is exemplified by the **Mond process** for the refining of nickel. Nickel when heated in a stream of carbon monoxide forms volatile nickel carbonyl, $Ni(CO)_4$. The carbonyl vapour when subjected to still higher temperature

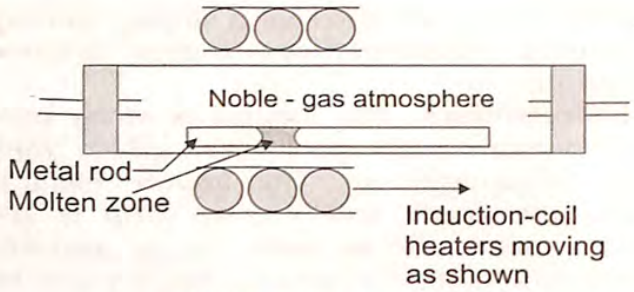


Fig.10.9 Zone refining

undergoes thermal decomposition giving pure metal.

$$\underset{\text{Impure}}{Ni} + 4CO \xrightarrow{330\text{–}350K} \underset{\text{Nickel carbonyl}}{Ni(CO)_4}$$

$$\underset{\text{Pure}}{Ni} + 4CO \xleftarrow{450\text{–}470K} Ni(CO)_4$$

Another process, given by van Arkel is very similar to the above in which zirconium (or titanium) is heated in iodine vapour at about 870 K to form volatile ZrI_4. The latter when heated over a tungsten filament at 2075K decomposes to give pure zirconium.

$$\underset{\text{Impure}}{Zr} + \underset{(I_2 \text{ vapour})}{2I_2} \xrightarrow{870K} \underset{\text{(Vapour)}}{ZrI_4}$$

$$\underset{\text{(Pure)}}{Zr} + 2I_2 \xleftarrow[\text{Tungesten filament}]{2075} ZrI_4$$

(vi) Chromatographic method : The principle of separation or purification by chromatography is that the various components of a mixture are differently adsorbed on an adsorbent. In column chromatography an adsorbent (e.g. Al_2O_3) is packed in a glass column. The mixture to be separated or purified, taken in a suitable solvent, is applied on the top of the column. The components of the mixture get adsorbed on the column. They are then eluted out with a suitable eluent (solvent). The weakly adsorbed component is eluted first followed by the more strongly adsorbed and so on. The method is especially suitable for such elements which are available only in minute quantities and the impurities are not very much different in their chemical behaviour from the element to be purified.

10.9 THERMODYNAMICS OF METALLURGY

Thermodynamic considerations are very important in metallurgical processes. These can help in deciding the temperature and the choice of reducing agents in the reduction processes. However, you will study these aspects after reading the second law of thermodynamics in Class XII. In Unit 5, we have considered only the *enthalpy of reaction* which alone is inadequate to give the direction of the process at constant temperature and pressure. Standard Gibbs free energy change $\Delta G^\ominus$ is defined in terms of enthalpy and entropy changes. The Gibbs free energy change decides the direction of the process at constant temperature and pressure.

SUMMARY

Most of the matter in the universe consisted of H and He in the beginning. As a result of vigorous nuclear reactions all other elements were formed subsequently. The earth formed as a result of condensation of elements is divided into different zones, such as core, mantle, crust, hydrosphere and atmosphere. Elements with low atomic numbers constitute major portion of the earth's crust, elements with even numbers being more abundant than those with odd numbers.

Elements occur in the earth's crust either in the native state or in the combined forms. Naturally occurring substances in the earth's crust are known as *minerals* and those which can be profitably used as a source of some desired materials are termed as *ores*. The earthy material present in an ore is known as gangue. There are several methods for concentration of ores. The choice of a method depends on the nature of the ore.

The concentrated ore is subjected to roasting/smelting so as to get rid of gangue and also to get the oxide form most of the cases. Thereafter the ore is subjected to a

reduction process.

The choice of a reducing agent is decided by several factors. Apart from energetics, the availability of the reductant and practicability of the method are important considerations.

The crude metals are finally refined for which, as per requirement, several methods are available.

A summary of the extraction of some common metals is presented as follows.

Metals	Occurrence	Extraction Method	Remark
Lithium	Spodumene, $LiAlsi_2O_6$ Lepidolite, $(Li, Na, K)_2 Al_2(SiO_3)_3 . F(OH)$	Electrolysis of fused LiCl/KCl	Because of their high reactivity they are extracted under anhydrous conditions.
Sodium	Rock-salt, NaCl Feldspar, $Na_3AlSi_3O_8$	Electrolysis of fused NaCl or NaCl/ $CaCl_2$	
Magnesium	Carnallite, $KCl.MgCl_2 . 6H_2O$ Magnesite, $MgCO_3$	Electrolysis of fused MgO or $MgCl_2$/KCl. Carbon reduction of MgO.	Carbon reduction is not possible with alkaline earths as a carbide is formed with them.
Calcium	Limestone $CaCO_3$ Dolomite, $MgCO_3 . CaCO_3$ Gypsum, $CaSO4 . 2H_2O$.	Electrolysis of fused $CaCl_2/CaF_2$	
Copper	Copper pyrites, $CuFeS_2$, Cuprite, Cu_2O Malachite, $CuCO_3.Cu(OH)_2$	Roasting of sulphide partially and reduction $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$	It is self reduction in a specially designed converter. Sulphuric acid leaching is also employed.
Aluminium	Bauxite, $Al_2O_3.2H_2O$ Cryolite, Na_3AlF_6 Aluminosilicates	Electrolysis of Al_2O_3 dissolved in molten cryolite or in Na_3AlCl_6	A good source of electricity is needed in the extraction of Al.
Zinc	Zinc blende or Spharelite, ZnS Calamine, $ZnCO_3$	Roasting and then reduction with C.	The metal may be purified by fractional distillation.
Lead	Galena, PbS	Roasting of the sulphide ore and then reduction of the oxide.	
Tin	Cassiterite, SnO_2	Carbon reduction of the oxide.	Magnetic separation is employed as the impurities in this case are magnetic.
Silver	Argentite, Ag_2S Horn silver, AgCl	Sodium cyanide leaching of the sulphide ore and finally replacement of Ag by Zn.	
Gold	Native, small Amounts in many ores such as those of copper and silver.	Cyanide leach, same as in case of silver.	
Chromium	Chromite, $Cr_2O_3.FeO$	Si or Al reduction of the oxide (Alumino-thermic process).	

EXERCISES

10.1 Why is Fe an abundant element on earth, and why are the elements with higher atomic numbers increasingly rare?

10.2 Copper and silver are below hydrogen in electrochemical series and yet they are found in the combined state as sulphides in nature. Comment.

10.3 Describe the principle of froth flotation process. What is the role of a stabilizer and of a depressant? Give one example each.

10.4 Describe the principle of each of the following processes in detail.
(a) Mond's process
(b) Zone refining
(c) Electrolytic refining

10.5 You are provided with samples of some impure metals such as zinc, copper and germanium. Which methods would you recommend for the purification of each of these metals?

10.6 Name the chief forms of the occurrence of the following in the earth's crust:
(a) aluminium (b) calcium (c) sodium (d) lead

10.7 Discuss some of the factors which need consideration before deciding on the method of extraction of metal from its ore.

10.8 The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with examples.

10.9 Which is a better reducing agent at 710°C, C or CO?

10.10 Indicate the temperature at which carbon can be used as a reducing agent for FeO.

10.11 Is it true that under certain conditions Mg can reduce SiO_2 and Si can reduce MgO?

10.12 Giving appropriate examples (at least three), explain how the reactivity of a metal is related to its mode of occurance in nature.

10.13 Name three metals which are obtained by the reduction of their oxides though they do not occur as such in the earth's crust.

10.14 Outline the principles of refining of metals by the following methods:
(i) Electrolytic refining
(ii) Zone refining
(iii) Vapour phase refining

10.15 Predict the modes of occurrence of the following three types of metals:
(i) Highly reactive (e.g. Na)
(ii) Moderately reactive (e.g. Fe)
(iii) Noble metal (e.g. Au)

10.16 How do non-metals occur in nature? How are they extracted/isolated from their natural sources?

10.17 Name the processes from which chlorine is obtained as a bye product. What will happen if an aqueous solution of NaCl is subjected to electrolysis?

10.18 Name the chief ores of tin, iron and aluminium. What methods are employed for the concentration/purification of their ores?

10.19 Name three ores which are concentrated by froth-floatation process. What is meant by a depressant?

10.20 What is the thermodynamic consideration in the choice of a reducing agent in metallurgy?

10.21 Carbon monoxide is more effective agent than carbon below 983K but above this temperature the reverse is true. How would you explain this?

10.22 Describe the principle of extraction of each of the following :
(i) Sn from SnO_2
(ii) Zn from ZnO
(iii) Cr from Cr_2O_3

10.23 Which metals are generally extracted by the electrolytic processes? What positions these metals generally occupy in the periodic table?

10.24 Name the main steel plants which are operated by the Steel Authority of India.

10.25 Name the metals which are associated with the following terms in their extraction from their ores:
(i) Bessemer's converter
(ii) Blast furnace
(iii) Alumino thermic process
(iv) Magnetic seperation

10.26 What do you understand by the following terms?
(i) Roasting
(ii) Calcination
(iii) Smelting

10.27 Which method would you suggest for the separation of the metals in the following mixtures?
(i) Zinc and iron
(ii) Copper and magnesium
(iii) Rare earths
Give reasons for your choice.

UNIT 11

HYDROGEN

Objectives

After studying this Unit, you will be able to

- understand the unique position of hydrogen in the periodic table.
- know about the occurrence and isotopes of hydrogen.
- understand the methods of preparation (including commercial preparation), properties, reactions and uses of dihyrogen.
- learn about saline, interstitial and molecular hydrides.
- know the structure of water and its physical and chemical properties.
- understand the difference between hard and soft water, and learn about water softening and heavy water.
- know the preparation, properties and uses of hydrogen peroxide.
- learn about hydrogen economy and use of liquid hydrogen as a fuel.

"Hydrogen forms more chemical compounds than any other element."

HYDROGEN

Hydrogen is the simplest among the known elements. In the hydrogen atom, there is one proton and one electron. The atomic form exists only at high temperatures. Normal elemental hydrogen is the diatomic molecule, called dihydrogen, H_2.

The box below lists the forms, isotopes, allotropes of hydrogen.

Symbol	:	H
Atomic Number, Z	:	1
Electronic configuration	:	$1s^1$
Isotopes	:	Protium, ^1H Deuterium, ^2H or D Tritium, ^3H or T
Allotropes	:	Orthohydrogen, o-H_2 Parahydrogen, p- H_2 [Also o-D_2, p-D_2, o-T_2, p-T_2]
Molecular forms	:	$^1H_2$, $^2H_2$ (D_2), $^3H_2$ (T_2), HD, HT, etc.
Ionic forms	:	H^-, H^+, H_2^+, H_3^+ .....H_{11}^+. [Also corresponding ionic forms of D and T].

11.1 UNIQUE POSITION OF HYDROGEN IN THE PERIODIC TABLE

As discussed in unit 4, the proper placement of hydrogen in the periodic table has been a subject of discussion in the past. Some chemists have argued for its grouping with the alkali metals while some other chemists have advocated for its inclusion with the halogens.

Harold C. Urey was born in Workerton, Indiana (U.S.A.). After graduation from the High School in Waterloo, Indiana, he taught three terms in country school, then entered the University of Montana and received the Bachelor of Science degree in zoology in 1917. His interest in physical and mathematical chemistry developed under stimulating influence of G.N. Lewis. He also got inspiration from Neils Bohr at the Institute of Theoretical Physics at Kopenhagen. In 1929, he was appointed Associate Professor of Chemistry at Colombia University where subsequently became Professor in 1934. Prof. Urey separated hydrogen isotope of atomic mass 2 by physical operations. The isotope was named as deuterium. It is widely used in various spheres of research and development. For this great contribution, he was awarded the Nobel Prize in 1934.

HAROLD C. UREY

Hydrogen with the electronic configuration, $1s^1$ can gain an electron to form the H^- ion with the stable noble gas configuration of helium ($1s^2$). It can also lose its electron to give the H^+ ion (the proton). Hydrogen, therefore has resemblance to the halogens as well as to the alkali metals which gain or lose an electron respectively to form univalent negative and positive ions with noble gas configurations. However, hydrogen with only one electron is different from the halogens as well as the alkali metals. Hydrogen has none of the metallic characteristics* and its resemblance to the halogens is only slight. The proton, H^+, has a very small size ($\sim 1.5 \times 10^{-3}$ pm) compared to normal atomic and ionic sizes of 50 to 220pm. It cannot exist freely and is always associated with other atoms or molecules. The ionization enthalpy of hydrogen (1312 kJ mol^{-1}) is very high compared to the alkali metals. It forms numerous covalent compounds. Dihydrogen, H_2, itself is a covalent molecule.

Hydrogen with so many unique characteristics is, therefore best placed separately in the periodic table of elements. (See Unit 4)

11.2 DIHYDROGEN, H_2

11.2.1 Occurrence

Hydrogen is the most abundant element in the universe.(70% of the universe's total mass). The giant planets Jupiter and Saturn consist mostly of hydrogen. Similarly about half the mass of the sun and some other stars is made up of hydrogen. It is the third most abundant element on the surface of the globe. In the combined form it constitutes 15.4% of the earth's crust and the oceans. Earth does not possess enough gravitational pull to retain the light H_2 molecules, so it is not found in our atmosphere.

In the crustal rocks it is 10^{th} in the order of abundance ~ 0.15% by weight.

11.2.2 Isotopes of Hydrogen

The three isotopes of hydrogen are protium $\left({}_1^1H\right)$, deuterium $\left({}_1^2H \text{ or } D\right)$ and tritium $\left({}_1^3H \text{ or } T\right)$.

The predominant form is protium whose atoms are made up of a single proton and a single electron. The deuterium nucleus is made up of a proton and a neutron, giving it a mass number of 2. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD.

The tritium $\left({}_1^3H\right)$ concentration is about 1 atom per 10^{18} atoms of protium. It is radioactive and emits low energy β- particles ($t_{1/2}$ 12.33y).

The characteristic atomic properties of the three isotopes are given in Table 11.1.

Table11.1 Atomic Properties of Isotopes of Hydrogen

Property	H	D	T
Relative atomic Mass	1.007825	2.014102	3.016049
Nuclear spin quantum number	½	1	½
Radioactive stability	Stable	Stable	β, $t_{½}$ = 12.33y

The atomic properties of the three isotopes indicate that they can be used in isotope

* *Hydrogen under very very high pressures is expected to behave like a metal. Recent reports from America have confirmed this possibility.*

studies, radioactive tracer studies (T) and nmr spectroscopy.

Table 11.2 Physical Properties of Dihydrogen and Dideuterium

Property	H_2	D_2
Melting point /K	13.957	18.73
Boiling point /K	20.39	23.67
Enthalpy of fusion/kJ mol^{-1}	0.117	0.197
Enthalpy of vapourization/kJ mol^{-1}	0.904	1.226
Enthalpy of dissociation/kJ mol^{-1} (at 298.2K)	435.88	443.35
Inter-nuclear distance /pm	74.14	74.14

11.3 PREPARATION AND COMMERCIAL PRODUCTION OF HYDROGEN

11.3.1 Small Scale Preparation of Dihydrogen

There are a number of methods for preparing dihydrogen from metals and metal hydrides but in the laboratory it is generally prepared by the reaction of zinc with dilute hydrochloric acid.

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

11.3.2 Commercial Production of Dihydrogen

The commonly used processes are:

Electrolysis of acidified water, using platinum electrodes, is employed for the bulk preparation of dihydrogen.

$$2H_2O(l) \xrightarrow[\text{Traces of acid/base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

(i) Hydrogen of high purity (>99.95%) is obtained by electrolysing warm aqueous barium hydroxide between nickel electrodes.

(ii) Reaction of steam on hydrocarbons or coke at high temperatures

$$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Catalyst}]{1270K} nCO + (2n+1)H_2$$

e.g. $$CH_4 + H_2O \xrightarrow{1270K} CO + 3H_2$$

$$C_3H_8(g) + 3H_2O(g) \xrightarrow[\text{Catalyst}]{1270K} 3CO(g) + 7H_2(g)$$

$$C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$$

CO is converted to CO_2 by passing the gases and steam over an iron oxide or cobalt oxide catalyst at 673K resulting in the generation of more H_2

$$CO + H_2O \xrightarrow[\text{Catalyst}]{673K} CO_2 + H_2$$

This is called the **water-gas shift reaction**

(iii) Relatively smaller quantities of dihydrogen (1-17 $m^3 h^{-1}$) are obtained by passing a 1:1 molar mixture of vaporised methanol and water over a **"base-metal chromite" type catalyst** at 673K. The mixture of hydrogen and carbon monoxide obtained is made to react with steam to give CO_2 and more hydrogen.

$$CH_3OH \xrightarrow[\text{Catalyst}]{673K} CO + 2H_2$$

$$CO + H_2O \xrightarrow[\text{Catalyst}]{673K} CO_2 + H_2$$

(iv) It is also produced as a by-product of the brine electrolysis process for the manufacture of chlorine and sodium hydroxide (See unit 12).

Presently ~ 77% of the industrial hydrogen produced is from petro-chemicals. 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

11.4 PROPERTIES OF DIHYDROGEN

11.4.1 Physical Properties

Dihydrogen* is a colourless, odourles and tasteless gas. The values of its physical parameters along with those for dideuterium are given in Table 11.2. It can be seen that the values for dideuterium are substantially higher as compared to diprotium. The relatively inert behaviour of dihydrogen at room temperature is due to the high enthalpy of H-H

* *The term **dihydrogen** is used for the H_2 molecule while referring to the isotopic mixture with natural abundance for H and D. For H_2 the correct term is **diprotium**. Similarly **proton** is used for H^+ and **hydron** is used in relation to the isotopic mixture.*

bond, being the highest for a single bond between any two elements. Significant decomposition of H_2, into its atoms occurs only above 2000K (0.081%) which increases to 95.5% at 5000K.

Dihydrogen has two nuclear spin isomers called ortho and para–dihydrogen. Their nuclei possess parallel and anti-parallel nuclear spins respectively. (Fig.11.1).

ortho-hydrogen (Parallel nuclear spins) para-hydrogen (Antiparallel nuclear spins)

Fig.11.1

The two isomers have 1 and 0 nuclear spin respectively. Conversion of one isomer into the other is a slow process. Para-hydrogen with lower energy is favoured at low temperatures. Above zero K, the equilibrium concentration of the ortho isomer increases until a limiting 3:1 proportion of ortho: para is established. Whereas it is possible to obtain pure para–hydrogen, it is never possible to obtain a sample containing more than 75% of ortho-hydrogen.

The physical properties of dihydrogen are not significantly affected by nuclear spin isomerism. However some of the notable differences are: (i)The thermal conductivity of para-hydrogen is 50% greater than that of the ortho-hydrogen and (ii)The melting point of para-hydrogen is 0.15K below that of hydrogen containing 75% o-H_2.

11.4.2 Chemical Properties

- Dihydrogen H_2 combines with halogens (X) to give hydrogen halides (HX). While the reaction with fluorine takes place even in the dark; with iodine a catalyst is required:

  $H_2(g) + X_2(g) \rightarrow 2HX(g)$ (X= F,Cl,Br,I)

- With dioxygen, dihydrogen forms water. The reaction is strongly exothermic.

  $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$; $\Delta H^{\ominus} = -285.9\ kJ\ mol^{-1}$

  With dinitrogen it forms ammonia.

  $$N_2(g) + 3H_2(g) \xrightarrow[Fe]{673\ K,\ 200\ atm} 2NH_3(g);$$

  $$\Delta H^{\ominus} = -92.6\ kJ\ mol^{-1}$$

  The method is used for the manufacture of ammonia by the Haber process (Unit 13).

- Dihydrogen reacts with many metals and non-metals at higher temperatures to yield the corresponding hydrides (see section 11.6 for details)

  $H_2(g) + 2M(s) \rightarrow 2MH(s)$

  (where M represents an alkali metal)

  Dihydrogen reduces some metal ions in aqueous solution, for example :

  $Pd^{2+}(aq) + H_2(g) \rightarrow Pd(s) + 2H^+(aq)$

- Oxides of metals (less active than iron) get reduced by dihydrogen to the corresponding metals:

  $yH_2(g) + M_xO_y(s) \rightarrow xM(s) + yH_2O(l)$

- The hydrogenation of many organic compounds using heterogeneous and homogeneous catalysis constitute important industrial processes. For example: (a) the hydroformylation of olefins to aldehydes.

  $RCH = CH_2 + H_2 + CO \rightarrow RCH_2\ CH_2\ CHO$

  which is further reduced to alcohol by the reaction

  $RCH_2\ CH_2\ CHO + H_2 \rightarrow RCH_2\ CH_2\ CH_2\ OH$

  (b) The hydrogenation of vegetable oils to solid edible fats (margarine and vanaspati).

Hydrogenation is used for the conversion of polyunsaturated oils into edible fats. Polyunsaturated vegetable oils have too many C=C bonds which undergo oxidation and the oil becomes unpleasent in taste, that is, it becomes rancid. Hydrogenation reduces the number of double bonds but does not completely eliminate them. Under controlled conditions, edible oils and margarine can be prepared by hydrogenation of vegetable oils like soyabean, corn, cotton seed oils. Nickel is used as the catalyst. Vanaspati— an edible cooking medium is prepared on a large scale in India by the hydrogenation process.

11.5 USES OF DIHYDROGEN

- The most important use of dihydrogen is in the manufacture of ammonia by Haber process;

  $$N_2(g) + 3H_2(g) \overset{673K/200atm}{\rightleftharpoons} 2NH_3(g)$$

- Dihydrogen is used in the manufacture of bulk

organic chemicals, particularly methanol:

$$CO(g) + 2H_2(g) \xrightarrow[\text{Catalyst}]{\text{Cobalt}} CH_3OH(l)$$

- Direct reaction of dihydrogen with chlorine is used for the preparation of hydrogen chloride:

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$$

- It is used for the manufacture of metal hydrides. (See section 11.6)
- In metallurgical processes, it is used to reduce heavy metal oxides to metals (See Unit 10).
- An important use of dihydrogen is in the atomic hydrogen and oxy-hydrogen torches for cutting and welding. Dihydrogen is dissociated with the help of an electric arc and the hydrogen atoms obtained are allowed to recombine on the surface to be welded. High temperature of 4000K is generated.

Other uses of dihydrogen are: as rocket fuel in space research; in bubble chambers as liquid hydrogen for the study of high energy particles; and in a fuel cell (Section 11.11).

11.6 HYDRIDES

Hydrogen forms binary hydrides of the type MH_x or $M_m H_n$ with:

- All main group elements except the noble gases and probably indium and thallium
- All lanthanoids and Actinoids
- Transition metals – Sc, Y, La, Ac, Tc, Zr, Hf and to a lesser extent V, Nb, Ta, Cr, Cu and Zn. Palladium hydride has been extensively studied.

The hydrides are classified into three categories:

(i) Saline Hydrides/ [Ionic Hydrides]
These are compounds of hydrogen with most of the *s*-block metals. They are non-volatile, non-conducting, crystalline solids. They are also referred to as 'salt-like' hydrides. However BeH_2 and MgH_2 have covalent polymeric structures.

(ii) Metallic Hydrides/ [Interstitial Hydrides]
These hydrides are formed by d-block and *f*-block metals. They are non-stoichiometric and show electric conduction.

(iii) Molecular Hydrides/[Covalent Hydrides]
Most of the hydrides of *p*-block elements which are volatile molecular compounds are placed in this category of hydrides.

11.6.1 The Saline or Salt-like Hydrides

The binary hydrides of alkali metals (LiH, NaH, KH, RbH, CsH) have rock-salt structures. The thermal stability of alkali metal hydrides decreases from LiH to CsH. The order of stability in the alkaline earth metal hydrides is: $CaH_2 > SrH_2 > BaH_2$.

Electrolysis of solutions of saline hydrides in molten alkali halides produces hydrogen gas at the anode which confirms the existence of the hydride, H^- ion.

$$2H^-(\text{melt}) \xrightarrow{\text{anode}} H_2(g) + 2e^-$$

Saline hydrides react explosively with water

$$NaH(S) + H_2O(aq) \rightarrow H_2(g) + NaOH(aq)$$

The fires so produced cannot be extinguished by carbon dioxide as it gets reduced by the hot metal hydride. Only sand is useful as it is a solid.

Alkali metal hydrides are used as reagents for preparing other hydride compounds, e.g. $LiAlH_4$ and $LiBH_4$.

While the hydrides of the heavier members of each group are supposed to have ionic bonds; there seems to be significant covalent character in the lighter metal hydrides (LiH, MgH_2 and BeH_2).

11.6.2 Metallic Hydrides/Interstitial Hydrides

d-block metals of groups 3,4,5 and the f-block metals form metallic hydrides. In group 6, Cr alone forms the hydride, CrH. The metals of groups 7,8 and 9 do not form hydrides. In fact, the region of the periodic table from group 7 to group 9 is referred to as the **Hydride Gap.** Examples of hydrides of groups 3 to 5 are:

ScH_2, YH_2, YH_3, LaH_2, LaH_3, TiH_2, ZrH_2, HfH_2, VH, VH_2, NbH, NbH_2, TaH.

The *f*-block elements form hydrides of limiting compositions of MH_2 and MH_3. All these compounds are, however non-stoichiometric.

Most metallic hydrides are conductors. They are non-stoichiometric, with variable compositions, for example : ZrH_x (with X = 1.30 to 1.75). TiH_x (X = 1.8 to 2).

Metallic hydrides can be used as hydrogen storage media. This property has potential for hydrogen storage and as a source of energy for vehicles. (See section 11.11).

11.6.3 Molecular Hydrides/Covalent Hydrides

Hydrogen forms molecular compounds with p-block elements: B, C, N, O, F, Si, P, S, Cl, Ga, Ge, As, Se, Br; In, Sn, Sb, Te, I; Tl, Pb, At. Familiar examples are CH_4, NH_3, H_2O and HF. The systematic names of molecular hydrides are usually formed from the name of the element and the suffix–ane, as in **phosphane** for PH_3. However common names like phosphine, water and ammonia have been used for such a long time in chemistry that scientists are generally reluctant to adopt their systematic names like phosphane, (PH_3), **oxidane** (H_2O) and **azane** (NH_3).

Molecular hydrides are further classified according to the relative numbers of electrons and bonds in their Lewis structures. Thus we have **electron-deficient, electron-precise and electron-rich** molecular hydrides exemplified by B_2H_6, CH_4 and NH_3 respectively.

An electron-deficient molecular hydride has too few electrons for writing its conventional Lewis structure. Diborane (B_2H_6) is an example. (See unit 13)

Electron – precise compounds are formed by the elements of group 14. The molecules are tetrahedral, for example CH_4. The bond distance increases on going down the group. Ammonia and water are examples of **electron-rich** hydrides. The excess electrons being present as lone pairs of electrons(ammonia-one lone pair; water-2 lone pairs). The presence of lone pairs and the highly electronegative atoms like nitrogen, oxygen and fluorine in electron-rich hydrides result in hydrogen bond formation. Presence of hydrogen bonds lead to high boiling points, high permittivities and aggregation in such compounds. Thus water, ammonia and hydrogen fluoride which are strongly hydrogen bonded species show all these characteristics.

11.7 WATER

Water is the most common, abundant and easily obtainable of all chemical compounds. It is a crucial compound for man's survival. It can be easily transformed from liquid to solid and to gaseous states. It is a solvent of great importance and is the most studied of all chemical compounds.

The distribution of water over the earth's surface is not uniform. The desert regions have no permanent surface water while the oceans cover vast areas 1.61×10^8 km^2 i.e. 78% of the earth's surface. They contain 97% of the available water. Less than 2.7% of the total surface water is fresh and most of it is locked in the Antarctic ice cap and in the Arctic. Antarctic ice cap covers 1.5×10^7 km^2. It contains $2.5 - 2.9 \times 10^7$ km^3 of fresh water. Fresh water lakes contain 1.25×10^5 km^3 of water, more than half of which is in the four largest lakes: Baikal (26000 km^3); Tanganyika (20000 km^3); Nayassa (13000 km^3) and Superior (12000 km^3). There are other innumerable smaller lakes, springs and rivers. Purification and re-cycling of water is now a major industry. The production of fresh water from sea and other saline waters has been commer-cialised.

The estimated world water supply is given in Tables 11.3.

Table 11.3

Source	Vol/10^3 km^3	% of Total
Oceans	1348000	97.33
Saline Lakes and Inland seas	105	0.008
Polar ice and glaciers	28200	2.04
Ground water	8450	0.61
Lakes	125	0.009
Soil Moisture	69	0.005
Atmospheric water vapour	13.5	0.001
Rivers	1.5	0.0001

11.7.1 Physical Properties of Water

Water is a colourless and volatile liquid. It has many unusual properties. Some of the physical properties of water, H_2O and heavy water, D_2O are listed in Table 11.4.

The peculiar properties of water in the condensed phases (liquid and solid state) are due to the presence of extensive hydrogen bonding between water molecules (unit 2). The abnormally high freezing point, boiling point, heat of vaporisation and heat of fusion (compared to the hydrides of other elements of

Table 11.4 Some Physical Properties of H_2O and D_2O

Property	H_2O	D_2O
Molecular mass (g mol $^{-1}$)	18.0151	20.0276
Melting point/K	273.0	276.8
Boiling point/K	373.0	374.4
Enthalpy of formation/kJ mol $^{-1}$	-285.9	-294.6
Enthalpy of vaporisation (373 K)/kJ mol $^{-1}$	40.66	41.61
Enthalpy of fusion/kJ mol $^{-1}$	6.01	--
Temp. of max. density/g cm $^{-3}$	276.98	284.2
Density (298K)/g cm $^{-3}$	1.0000	1.1059
Viscosity/centipoise	0.8903	1.107
Dielectric constant	78.39	78.06
Electrical conductivity (293K/Ohm $^{-1}$ cm $^{-1}$)	5.7 x 10 $^{-8}$	--

the same group of the periodic table, e.g., H_2S, H_2Se) are due to hydrogen bonding. Water has a higher specific heat, thermal conductivity and surface tension than most other liquids. These properties allow water to play a vital role in the biosphere. The high heat of vaporisation and the high heat capacity of water are responsible for moderation of the climate and body temperature of living organisms. Water is an excellent solvent for transportation of ions and molecules needed for plant and animal metabolism. Even covalent organic compounds like alcohols and carbohydrates have a high solubility in water because of their ability to form hydrogen bonds with water. Under very high pressure and temperature water behaves as a non-polar solvent and dissolves organic compounds while common inorganic salts are not dissolved.

When water freezes it forms ice – the crystalline form of water. Nine structurally different forms of ice are known. At atmospheric pressure ice crystallizes in the normal hexagonal form. I_h, but at very low temperatures it condenses to cubic form. Ice (I_h) has lesser density than the liquid phase with which it is in equilibrium. This property is of crucial significance for the preservation of aquatic life.

Many salts crystallize from aqueous solutions as hydrated salts. Such association of water is essentially of five types: **co-ordinated water, hydrogen bonded water, Lattice water, zeolitic water and clathrate water.**

11.7.2 Structure of water

The formation and structure of the water molecule have been discussed in detail in Unit-6. We may recapitulate that water in the gas phase is a bent molecule with a HOH bond angle of 104.5^0 and O-H bond length of 95.7 pm as shown in Fig.11.2(a).

Because of the high electronegativity of oxygen, water molecule is highly polar [Fig.11.2(b]. In the liquid phase the water molecules are held together by hydrogen bonds. Liquid water consists of aggregates of varying number of water molecules held together by hydrogen bonds in a dynamic equilibrium.

A remarkable characteristic of water is that in solid form, ice, is less dense than the liquid form. Consequently an ice cube floats in water. The density of almost all other substances in their solid state is greater than in liquid state. Many polar molecules like HF, NH_3 and H_2O form

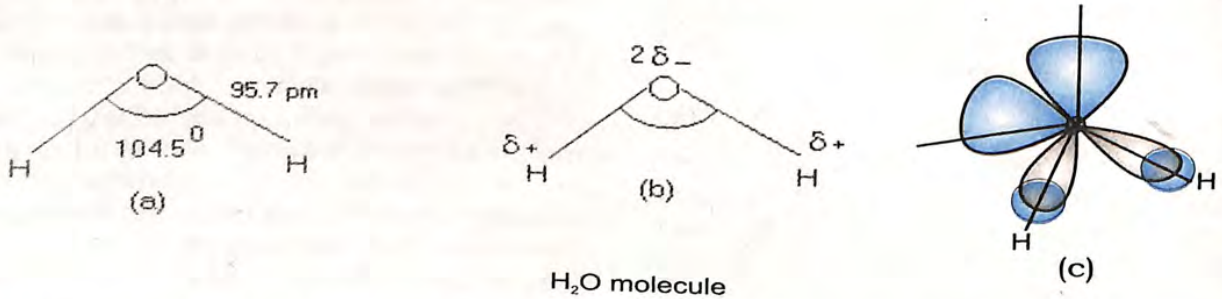


Fig.11.2 (a) The bent structure of water; (b) the water molecule as a dipole and (c) the orbital overlap picture in water.

inter-molecular hydrogen bonds. However there is a difference between water and other such molecules. The water molecules are joined together in an extensive three-dimensional network in which each oxygen atom is bonded to four hydrogen atoms two by hydrogen bonds and two by normal covalent bonds in a near tetrahedral configuration. This situation does not exist for molecules like NH_3 and HF.

Ice has a highly ordered three-dimensional hydrogen bonded structure (Fig.11.3), which has got open spaces. This is responsible for the low density of ice – a fact of great ecological significance. The ice layer, formed on the surface of a lake, for example, in winter, does not sink to the bottom. It, infact provides thermal insulation for the water below it and this ensures the survival of the aquatic life.

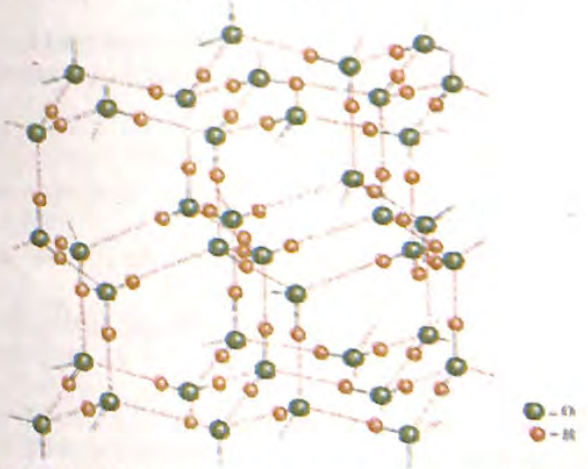


Fig.11.3 *The three-dimensional structure of ice. Each oxygen atom is bonded to four hydrogen atoms. The covalent bonds are represented by shorter full lines, and the weaker hydrogen bonds by longer broken lines between O and H atoms.*

11.7.3 Chemical Properties of Water

Water shows a varied and unique chemical behaviour.

- It has the ability to act as an acid or a base, in the Bronsted sense, that is, it behaves as an amphoteric substance. It can, for example, act as an acid towards ammonia;

  $H_2O(l) + NH_3(aq) \rightarrow OH^-(aq) + NH_4^+(aq)$

  And as a base towards H_2S;

  $H_2S(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HS^-(aq)$

In general water can act as a base towards acids stronger than itself and as an acid towards a base stronger than it. The auto-protolysis of water represented by:

$$\underset{\text{acid 1}}{H_2O(l)} + \underset{\text{base 2}}{H_2O(l)} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+(aq)} + \underset{\text{base 1}}{OH^-(aq)}$$

is thus of great importance in acid-base chemistry. (See Unit 8).

- Another important class of reactions in aqueous chemistry are the oxidation - reduction reactions. Water is reduced to H_2 by metals with E° value of the redox couple M^{n+}/M below/ = - 0.41V

  $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$;

  $E^\circ = -0.41V$ for $[OH^-] = 10^{-7}M$

  Water can also be oxidized as shown by the equation

  $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$

  $E^\circ = +0.82$ V for $[H^+] = 10^{-7}$ M

  Some typical examples of this type of reaction are oxidation of H_2O to O_2 during photosynthesis and oxidation by fluorine.

  $2F_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$

- Water with a high dielectric constant has a very strong solvating character. It acts as an excellent solvent. Because of the great affinity of many elements for oxygen, hydrolysis of ionic or covalent compounds occurs in water, e.g.,

  $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

  $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(OH_2)_6]^{3+}(aq) + 3Cl^-(aq)$

  $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$

  $Ca_3N_2(s) + 6H_2O(l) \rightarrow 3Ca(OH)_2(aq) + 2NH_3(g)$

- Water forms **hydrates** with metal salts. There are three main types of hydrates:
  (i) Compounds in which water molecules are coordinated to a metal ion (complex compounds) e.g.,

  $[Ni(OH_2)_6]^{2+}(NO_3^-)_2$; $[Fe(OH_2)_6]^{3+}$ 3Cl ;

  $[Cr(OH_2)_6]^{3+}$ 3Cl

  (ii) Compounds in which water molecule may be hydrogen bonded to oxygen containing anions, e.g. $CuSO_4$. $5H_2O$.
  (iii) Water is present in some compounds as interstitial water, i.e it occupies the intersticies (interstitial sites) in the crystal lattice; e.g. $BaCl_2$. $2H_2O$.

11.8 HARD AND SOFT WATER

Natural water is classified as **Hard** and **Soft** depending on the nature of substances dissolved in it. Water, containing soluble calcium and magnesium salts like bicarbonates, chlorides and sulphates is called **Hard Water**. In such water soap does not lather as the sodium stearate changes to the corresponding calcium/ magnesium salt which precipitates out, e.g.,

$$2C_{17}H_{35}COONa + Ca^{2+}/Mg^{2+} \rightarrow (C_{17}H_{35}COO)_2 Ca/Mg \downarrow + 2Na^+$$

Water free from calcium/magnesium bicarbonate, chloride, sulphate is called **Soft Water**. It readily gives a lather with soap.

Apart from being unsuitable for laundry washing and dyeing, hard water is harmful for steam boilers. Over a period of time the inner surface of the boiler gets crusted with the so called **"boiler scale"** which is largely calcium sulphate, calcium carbonate and magnesium oxychloride. The deposition reduces the efficiency of the boiler and also damages it. It is therefore necessary to render the water soft before it can be used.

The hardness of water may be of temporary or permanent nature.

Temporary hardness is due to the presence of bicarbonates of calcium and magnesium. It can be removed by (i) boiling, when the soluble bircarbonates change to carbonates which being insoluble, get precipitated.

$$M(HCO_3)_2 \rightleftharpoons MCO_3 \downarrow + H_2O + CO_2 \uparrow ; M = Ca \text{ or } Mg$$

and (ii) Clark's process. Addition of a calculated quantity of lime which causes precipitation of calcium carbonate.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightleftharpoons 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightleftharpoons 2CaCO_3 + Mg(OH)_2 + 2H_2O$$

Permanent hardness is due to the presence of soluble calcium/magnesium sulphates/ chlorides. It cannot be removed by boiling. The softening may be carried out by treatment with sodium carbonate.

$$CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 \downarrow + Na_2SO_4$$

$$MgCl_2 + Na_2CO_3 \rightleftharpoons MgCO_3 \downarrow + 2NaCl$$

The removal of both temporary and permanent hardness of water can be effected by ion exchangers.

(i) *Zeolite/permutit* : By passing the hard water through a column of zeolite or hydrated sodium aluminum silicate called permutit, $NaAlSiO_4.3H_2O$. Due to ion-exchange, sodium in the silicate/zeolite gets exchanged for Ca^{2+}/Mg^{2+} ions and the water gets softened.

$$2NaAlSiO_4 + Ca^{2+} \rightleftharpoons Ca(AlSiO_4)_2 + 2Na^+$$

$$2NaAlSiO_4 + Mg^{2+} \rightleftharpoons Mg(AlSiO_4)_2 + 2Na^+$$

The zeolite/permutit can be regenerated by treatment with sodium chloride solution.

(ii) *Synthetic resins* : Hard water is mostly softened by using synthetic cation ion-exchangers. They are more efficient than zeolite and permutit. These cation exchangers are large organic molecules containing sulfonic acid, RSO_3-H groups.

The ion-exchange resin is first changed to the sodium from by treatment with NaCl solution and then used for softening of water.

$$2RNa^+ + M^{2+} \rightleftharpoons R_2M + 2Na^+$$

(where M^{2+} represents Ca^{2+}/Mg^{2+} and R is the resin anion).

The resin can be re-generated for further use by treatment with NaCl solution.

Pure de-mineralised (de-ionized) water, free from all soluble mineral matter is obtained by passing water successively through a cation ion-exchanger (in the H^+ form) and an anion-exchanger (in the OH^- form) for removal of cations and anions:

$$2RH^+ + M^{2+} \rightleftharpoons MR_2 + 2H^+$$

(R is the resin anion, M^{2+} is a cation)

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ . OH^-$$

$$RNH_3^+ OH^- + X^- \rightleftharpoons RNH_3^+X^- + OH^-$$

$$H^+ + OH^- \rightarrow H_2O$$

In the first exchange H^+ exchanges for Ca^{2+}, Mg^{2+}, Na^+ and other cations present in water and it becomes acidic. In the next exchange, anions like Cl^-, SO_4^{2-}, HCO_3^-, etc are replaced by OH^- ions which neutralize the H^+ ions set free in the first exchange. The water becomes neutral. The cation and anion exchange resin beds when exhausted are regenerated by treatment with dilute acid and NaOH respectively.

11.9 HYDROGEN PEROXIDE, H_2O_2

11.9.1 Preparation

(i) Hydrogen peroxide was first prepared by J,L,Thenard in 1818 by acidifying barium peroxide and removal of excess H_2O by evaporation under reduced pressure.

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$

$$BaO_2.\ 8H_2O\ (s) + H_2SO_4\ (aq) \rightarrow BaSO_4\ (s) + H_2O_2\ (aq) + 8H_2O\ (l)$$

(ii) By hydrolysis of peroxodisulphate obtained by electrolytic oxidation of acidified sulphate solutions at high current densities

$$2HSO_4^-(aq) \xrightarrow{\text{electrolysis}} HO_3SOOSO_3H\ (aq) \xrightarrow{\text{hydrolysis}} 2HSO_4^- + H_2O_2$$

This processes is now used only for the laboratory preparation of D_2O_2, e.g

$$K_2S_2O_8 + 2D_2O \rightarrow 2KDSO_4 + D_2O_2$$

(iii) Industrially, H_2O_2 is prepared by the auto-oxidation of 2-alkylanthraquinols. The process involves a cycle of reactions. The net reaction is the catalytic union of H_2 and O_2 to yield H_2O_2.

$$\text{2-ethylanthraquinol} \underset{H_2/Pd}{\overset{O_2(air)}{\rightleftharpoons}} \text{(Oxidised product)} + H_2O_2$$

The hydrogen peroxide formed (~ 1%) is extracted with water and concentrated to ~ 30% (by weight) by distillation under reduced pressure. It can be further concentrated to ~ 85% by careful distillation under low pressure. The remaining water can be frozen out to give pure H_2O_2.

11.9.2 Physical Properties of H_2O_2

In the pure state, H_2O_2 is an almost colourles (very pale blue), somewhat dense, less volatile liquid than water. The important physical characteristics of H_2O_2 are listed in Table 11.5.

H_2O_2 is miscible with water in all proportions and forms a hydrate $H_2O_2.\ H_2O$ (m.p 221K). A 30 percent solution is marketed as "100-volume" hydrogen peroxide, indicating that at S.T.P 100 volumes of oxygen are liberated per millilitre of the solution. Commercial H_2O_2 marketed as "10-volume" peroxide contains 3 percent H_2O_2.

11.9.3 Structure of H_2O_2

Hydrogen peroxide molecule has a non-planar structure. The molecular dimensions in the gas phase and solid phase are shown in Fig.11.4.

11.9.4 Chemical Properties of Hydrogen Peroxide

The oxidation state of oxygen in H_2O_2 is (1-), a value which lies in between the oxidation state values of oxygen in O_2 (zero) and H_2O (2-). Aqueous solutions of H_2O_2 spontaneously decompose:

$$H_2O_2(l) \rightarrow H_2O(l) + \tfrac{1}{2}\ O_2(g)$$

The decomposition occurs slowly but the presence of metal surfaces, traces of alkali (present in glass) strongly catalyze the reaction. It is also decomposed by exposure to light. H_2O_2 is therefore stored in wax-lined glass or plastic vessels in the presence of stabilizers like urea. Dust (even in very small quantities) induces explosive decomposition.

The chemistry of H_2O_2 is characterised by:

(i) Its ability to act as an oxidising agent or a reducing agent in both acidic and alkaline media:

(a) **Oxidising action in acid solution** : Some typical reactions are:

$$2FeSO_4(aq) + H_2SO_4(aq) + H_2O_2(aq) \rightarrow Fe_2(SO_4)_3(aq) + 2H_2O\ (l)$$

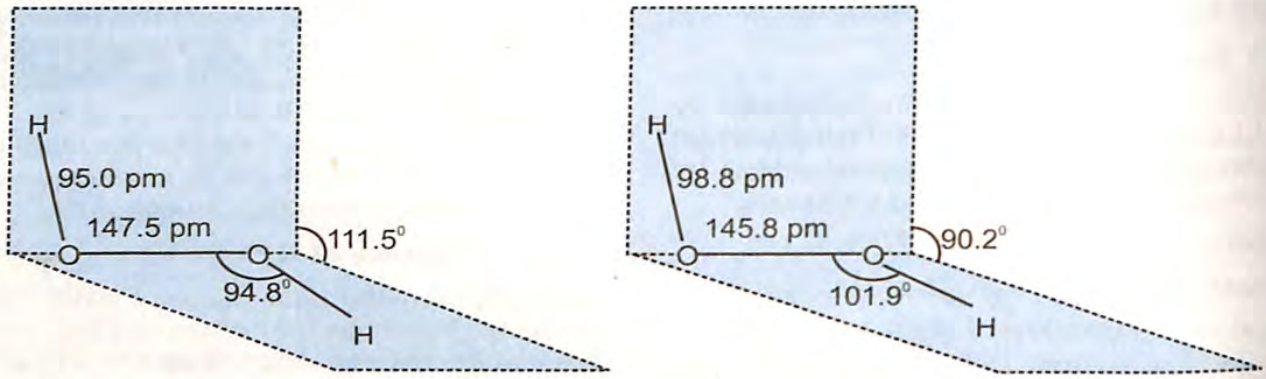
$$H_2SO_3(aq) + H_2O_2(aq) \rightarrow H_2SO_4(aq) + H_2O(l)$$

$$PbS(s) + 4H_2O_2(aq) \rightarrow PbSO_4(s) + 4H_2O(l)$$

(b) **Oxidising action in alkaline solution:**

Table 11.5 Physical characteristics of H_2O_2

Melting point /K	272.4	Density (liquid at 298K)/g cm^{-3}	1.4425
Boiling point (extrapolated) /K	423	Viscosity(290K)/centipoise	1.245
Vapour pressure (298K)/mmHg	1.9	Dielectric constant (298K)	70.7
Density (solid at 268.5K)/g cm^{-3}	1.6434	Electrical conductivity (298K)$\Omega^{-1}cm^{-1}$	5.1×10^{-8}



(a) Gas phase (b) Solid phase

Fig .11.4 *(a) H_2O_2 structure (gas phase) Dihedral angle 111.5°. (b) H_2O_2 (Solid phase at 110K). The dihedral angle is reduced to 90.2. The O-O distance is of a normal single bond.*

$$Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^-$$

(c) **Reducing action in acid solution**

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

$$HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$$

(d) **Reducing action in alkaline solution**

$$2Fe^{3+} + H_2O_2 + 2OH^- \rightarrow 2Fe^{2+} + 2H_2O + O_2$$

$$2KMnO_4 + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2KOH$$

$$Cl_2 + H_2O_2 + 2OH^- \rightarrow 2Cl^- + 2H_2O + O_2$$

(ii) H_2O_2 gives peroxo-metal complexes and peroxoacid anions.

11.9.5 Uses of H_2O_2

- The largest industrial use of H_2O_2 is as a bleach for textiles, paper pulp, straw, leather, oils, fats, etc.
- Domestically it is used as a hair bleach and as a mild disinfectant.
- It is extensively used to manufacture chemicals like sodium perborate and per-carbonate which are important constituents of high quality detergents.
- H_2O_2 is used for the production of epoxides, propylene oxide, and polyurethanes.
- It is also used in the synthesis of hydroquinone, pharmaceuticals (cephalosoporin) and food products like tartaric acid.
- A fast growing use of H_2O_2 is in environmental chemistry, for example in pollution control treatment of domestic and industrial effluents; oxidation of cyanides and the restoration of aerobic conditions to sewage wastes. This use has led to tremendous increase in the industrial production of H_2O_2.

11.10 HEAVY WATER, D_2O

Heavy water (for physical properties, refer to table 11.4) is obtained as a by-product in some fertilizer industries where hydrogen is produced by electrolysis of water.

Heavy water is used : as a moderator in nuclear reactors; in the study of mechanisms of chemical reactions involving hydrogen and its compounds and as the starting material for the preparation of a number of deuterium compounds, for example.

$$SO_3 + D_2O \rightarrow D_2SO_4$$

$$Al_4C_3 + 12D_2O \rightarrow 3CD_4 + 4Al(OD)_3$$

$$CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$$

11.11 HYDROGEN ECONOMY (USE OF LIQUID HYDROGEN AS A FUEL)

Responding to the realization that : i) the fossil fuels are limited; ii) the electricity cannot be stored and iii) the use of nuclear power has limitations, man has been prompted to search for alternative and feasible sources of energy.

A prospective alternative, in this regard, is what is popularly termed as **"Hydrogen Economy"**. The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous hydrogen.

The main aim and advantage of "hydrogen economy" is to transmit energy, not as electric

power, but in the form of hydrogen. This is expected to solve the problems associated with the storage and transmission of electricity.

The technology involves the production of bulk quantities of hydrogen electrically and its storage in liquid form in vacuum insulated cryogenic tanks (already in use for the space programmes in U.S.A). It is feasible to transport liquid hydrogen by road or rail tankers of (20,000 US gallons) capacity. It can also be stored in underground tanks and transported by pipe lines. Smaller storage units use metal alloy like $LaNi_5$, Mg – MgH_2,Ti–TiH_2 etc.

Use of hydrogen as an automobile fuel has many advantages:

- Release of greater energy per unit weight of fuel.
- Absence of polluting emissions like CO, CO_2, NO_x, SO_2, hydrocarbons, aldehydes and lead compounds.
- Combustion product is water with just some traces of nitrogen oxides.
- Internal combustion engines can be easily modified for use of hydrogen as fuel.
- Fuel cells for regeneration of electric power with conversion efficiency of 70-85% have been successfully operated commercially.

Nonelectrolytic production of hydrogen is a subject of intense study. The main principle involved in the process is the correct free-energy transfer to a water molecule for decomposing it. Some success has been achieved in this field and it is expected that the coming years will provide economically viable and safe sources of hydrogen for its usage as a general source of energy.

SUMMARY

Hydrogen is the simplest element known. It has a superficial resemblance to the alkali metals and the halogens. However its unique atomic structure, isotopic composition, the very small size of the proton, its inability to exist freely and the numerous covalent compounds formed by it justify a separate position for hydrogen in the periodic table.

Hydrogen, though the most abundant element in the universe, is not found in the earth's atmosphere. In the combined state it is the third most abundant element on the earth's surface.

Hydrogen is the only known element whose isotopes have the unique mass ratio of 1:2:3 (^1H : ^2H:^3H). The predominant form is ^1H (protium). ^2H or D (Deuterium) is present upto 0.0156% in terrestrial hydrogen mostly in the form of HD. ^3H or T (Tritium) is radioactive (emits β- particles; half-life, $t_{1/2}$ 12.33y). Deuterium and Trituim find use in isotopic and radioactive tracer studies respectively.

Dihydrogen is prepared industrially by the water-gas shift reaction, from petrochemicals and by the electrolysis of brine where it is obtained as a by-product.

Dihydrogen H_2, is a colourless, odourless, tasteless gas with a high heat of dissociation ~ 435.88 kJ mol^{-1}. This property is made use of in the atomic hydrogen torch which generates temperatures of ~ 4000k and is ideal for welding of high melting metals. Dihydrogen has nuclear spin isomers – ortho and para-hydrogen.

Among the chemical reactions of dihydrogen, notable ones are: formation of various hydrides, hydrogenation of organic compounds using homogeneous/heterogeneous catalysts and its reducing reactions.

The most important uses of dihydrogen are in the manufacture of ammonia (Haber process) and catalytic hydrogenation of unsaturated liquid vegetable oils to solid edible fats. To a smaller extent it finds use in the manufacture of bulk organic chemicals, particularly methanol and metal hydrides. In metallurgical processes, H_2 is used to reduce metal oxides. In space programmes it is used as a rocket fuel. There is a promising potential for its use as a fuel of the future (hydrogen economy).

Dihydrogen forms mainly three types of hydrides: saline or salt-like also called ionic

hydrides; metallic or interstitial hydrides and covalent or molecular hydrides. Alkali metal hydrides are used as reagents for preparing other hydride compounds. Metallic hydrides are used for the ultrapurification of hydrogen and as hydrogen storage media. Molecular or covalent hydrides like C_2H_6, NH_3, H_2O are very important compounds.

Water is the most common, abundant and easily obtainable substance. It is of great chemical and biological significance. Its transformation from liquid to solid and to gaseous states is easy. Water is the most studied of all chemical compounds. Water occupies the major part of earth. It is a colourles, mobile, volatile liquid with many unique properties. These particular properties in the liquid and solid phase are a result of extensive hydrogen bonding between water molecules. Thus water has a higher specific heat, thermal conductivity and surface tension than most of the other liquids. Because of these properties water plays a vital role in the biosphere. The water molecule has a bent structure. It behaves as an amphoteric substance. Water forms hydrates of different types.

The presence of hardness in water is an industrial hazard. Both temporary and permanent hardness can be removed by the use of (i) aluminosilicates like zeolites and (ii) synthetic organic ion-exchangers.

Hydrogen peroxide finds use as an industrial bleach and in pollution control. It can be prepared on a large scale by the auto-oxidation of 2-alkylanthraquinols. It has an interesting non-planar structure.

Heavy water, D_2O is manufactured by the electrolytic enrichment of normal water. It is essentially used as a moderator in nuclear reactors.

'Hydrogen economy' is basically use of liquid hydrogen as an alternate source of energy. The technology involves the production, transportation and storage of energy in the form of liquid hydrogen in bulk quantities. Hydrogen as a fuel has many advantages over conventional fuels in that it is not polluting and it can be stored and transported easily. There appears to be a great potential for use of hydrogen as a fuel of the future.

EXERCISES

11.1 Explain why hydrogen is best placed separately in the periodic table of elements?

11.2 What is understood by "Water gas shift reaction"? Discuss its use for the preparation of hydrogen.

11.3 Hydrogen forms compounds with elements having atomic numbers : 9, 11, 12 and 17. What are their chemical formulae? Compare their chemical behaviour.

11.4 What are metallic/interstitial hydrides? How do they differ from molecular hydrides?

11.5 Complete the following reactions
(i) $CaO\ (s) + H_2O\ (l) \rightarrow$
(ii) $Na_2O(s) + H_2O\ (l) \rightarrow$

11.6 Compare the structures of H_2O and H_2O_2.

11.7 Explain why hydrogen peroxide is stored in coloured/plastic bottles?

11.8 Describe the industrial applications of hydrogen dependent on:
(i) the heat liberated when its atoms are made to combine on the surface of a metal.
(ii) its effect on unsaturated organic systems in presence of a catalyst.
(iii) its ability to combine with nitrogen under specific conditions.

11.9 How is dihydrogen prepared
(i) from water by using a reducing agent?
(ii) in the laboratory in pure form?
(iii) from hydrocarbons?

11.10 Complete the following equations:
(i) $Fe(s) + H_2O(g) \rightarrow$
(ii) $PbS(s) + H_2O_2(aq) \rightarrow$
(iii) $MnO_4^-(aq) + H_2O_2(aq) \rightarrow$

11.11 Discuss the importance of heavy water in nuclear reactors.

11.12 How is heavy water prepared from normal water?

11.13 Explain why water has high boiling and melting points as compared to H_2S.

11.14 Describe the structure of the common form of ice.

11.15 Distinguish between: (i) hard and soft water and (ii) temporary and permanent hardness.

11.16 Discuss the principle and method of softening of hard water by organic ion exchange resins.

11.17 Explain the amphoteric nature of water

11.18 Show by proper chemical reactions how hydrogen peroxide can function both as an oxidising and a reducing agent?

11.19 What is understood by hydrogen economy?

11.20 Explain the correct context in which the following terms are used:
(i) diprotium (ii) dihydrogen
(iii) proton and (iv) hydron

11.21 Is it correct to say that hydrogen can behave as a metal? State the conditions under which such behaviour can be possible.

11.22 Name the isotopes of hydrogen. What is the importance of the heavier isotopes of hydrogen.

11.23 How many allotropes of dihydrogen are known? What is their importance?

11.24 Name the class of hydrides to which H_2O, B_2H_6, NaH and LaH_3 belong. What is understood by 'Hydride Gap'?

11.25 Hydrogen forms three types of bonds in its compounds. Describe each type of bonding using suitable examples.

11.26 Elements with atomic numbers 17 and 20 form compounds with hydrogen. Write the formulae of these two compounds and compare their chemical behaviour in water.

11.27 Give an example each of an ionic hydride and a covalent hydride.

11.28 Complete the following reactions:
(i) $CuO(s) + H_2(g) \rightarrow$
(ii) $CO(g) + H_2(g) \rightarrow$

11.29 Compare the chemical properties of H_2O and H_2O_2.

11.30 Describe some unusual properties of water.

11.31 What is the difference between hydrolysis and hydration?

11.32 What is understood by hydrogenation?

11.33 What are the advantages in using hydrogen as a fuel?

11.34 Ionic hydrides are frequently used to remove traces of water from organic compounds. What is the underlying basis of this process?
(Hint- H^- is a strong Bronsted base, high reactivity with water).

11.35 Although D_2O resembles H_2O chemically yet it is a toxic substance. Explain
(Hint – Slower rate of D^+ compared to H^+ in reactions involved in enzyme catalysis).

11.36 Why do lakes freeze from top towards bottom?

11.37 Why is ice less dense than water and what kind of attractive forces must be overcome to melt ice?

UNIT 12

THE s-BLOCK ELEMENTS

Objectives

After studying this Unit, you will be able to

- understand the general characteristics of the alkali metals.
- know about the extraction, properties, uses of lithium and sodium and industrially important compounds of sodium.
- know about the general characteristics of the alkaline earth metals and extraction, properties, uses of magnesium and important compounds of the alkaline earth metals including Portland cement.

In the block-wise division of the periodic table (Unit 4) the fo clearly identified blocks of elements are the *s*-block, the *p*-bloc the *d*-block and the *f*-block. In the build-up of atoms elemen belonging to a particular block receive their outermost electron in *s*-, *p*-, *d*- or *f*- orbitals. As the s-orbital can accommoda only two electrons, two groups (1 and 2) belong to the *s*-bloc of the periodic table. Group 1 consists of the elements : lithium sodium, potassium, rubidium, caesium and francium. The are collectively known as the **alkali-metals** after the Arab word *al-qis* meaning plant ashes since ashes of plants a particularly rich in the carbonates of sodium and potassium The elements of Group 2 include beryllium magnesium calcium, strontium, barium and radium. These elements wi the exception of beryllium are commonly known as the **alkali earth metals**.

Among the alkali metals sodium and potassium a abundant, lithium, rubidium and caesium have much low abundances (Table 12.1). Francium is radioactive; i longest-lived isotope ^{223}Fr has a half-life of only 21 minute Of the alkaline earth metals calcium and magnesium ra fifth and sixth in abundance respectively in the earth's crus Strontium and barium have much lower abundance Beryllium is rare and radium is the rarest of all comprisi only 10^{-10} per cent of igneous rocks (Table 12.2).

A regular trend is observed in the physical and chemic properties of the alkali metals with increasing atomic numbe The loosely held *s*-electron in the outermost valence shell these elements makes them the most electropositive meta which readily give ions, M^+. The relationship between th elements of the alkaline earth metals is similar to that betwee the alkali metals. Calcium, strontium, barium, with tw *s*-electrons in the valence shell, are also highly electropositiv They form M^{2+} ions.

Lithium and beryllium, the first elements of Group 1 an Group 2 respectively exhibit some properties which ar different from those of the other members of the respecti group. In these anomalous properties they resemble the secon

element of the following group. Thus lithium shows similarities to magnesium, and beryllium to aluminium in many of their properties. This type of diagonal similarity is commonly referred to as *diagonal relationship* in the periodic table. The diagonal relationship is due to similarity in ionic sizes and/or charge/radius ratios of the elements.

12.1 GENERAL CHARACTERISTICS OF THE ALKALI METALS

The alkali metals show regular trends in their physical and chemical properties more clearly than any other group of elements in the periodic table. These trends are discussed below.

12.1.1 Atomic Properties

(i) **Electronic configuration**. All these elements have one valence electron (ns^1) over and above the electronic configuration of noble gases (Table 12.1). The outermost s-electon is very well screened from the nuclear charge in these elements.

(ii) **Atomic and ionic size :** The alkali metal atoms have the largest sizes in a particular period in the periodic table. With increase in atomic number, the atoms become larger. The monovalent ions (M^+) are smaller than the parent atoms.

(iii) **Ionization enthalpy :** The ionization enthalpies of the alkali metals are considerably low and decrease down the group from Li to Cs. This is because the effect of increasing size outweighs the increasing nuclear charge.

12.1.2 Physical Properties

All the alkali metals are silvery white, soft and light metals. Because of large size, these elements have low density which increases generally down the group from Li to Cs. However, potassium is lighter than sodium. The melting and boiling points of the alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them. The alkali metals and their salts impart characteristic colours to an oxidising flame. The respective colours imparted are:

Metal	Li	Na	K	Rb	Cs
Colour	Crimson	Yellow	Violet	Red Violet	Blue
λ/nm	670.8	589.2	766.5	780.0	455.5

12.1.3 Chemical Reactivity

The alkali metals are highly reactive metals and the reactivity increases down the group.

(i) ***Reactivity towards water.*** Although lithium has the most negative E°, its reaction with water is considerably less vigorous than that of sodium which has the

Table 12.1 Atomic and Physical Properties of the Alkali Metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs
Atomic number Electron configuration	3 [He] $2s^1$	11 [Ne]$3s^1$	19 [Ar]$4s^1$	37 [Kr]$5s^1$	55 [Xe]$6s^1$
Ionization enthalpy / kJ mol^{-1}	520	496	419	403	376
Metallic radius/ pm	152	186	227	248	265
Ionic radius M^+/pm	76	102	138	152	167
m.p./ K	454	371	336	312	302
b.p/K	1615	1156	1032	961	944
Density/ g cm^{-3}	0.53	0.97	0.86	1.53	1.90
Standard Potentials E^0 M^+/M /V	3.04	-2.714	-2.925	-2.930	-2.927
Occurrence in lithosphere	18*	2.27**	1.84**	78-12*	2-6*

** ppm (part per million, ** percentage by weight)*

least negative E^0 among the alkali metals (see Table 12.1 for E^0 values). The reaction of sodium with water produces enough heat to melt it and hydrogen produced ignites in air. Other metals of the group with lower melting points react explosively with water. In all these cases the reaction with water occurs as :

$$2M + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2 \quad (M=\text{an alkali metal})$$

(ii) ***Reactivity towards air.*** The alkali metals tarnish in air due to the formation of an oxide or hydroxide on the surface. When heated in **excess of air**, the alkali metals form the oxides: Li_2O, Na_2O_2, KO_2, RbO_2 and CsO_2 respectively. The temperatures necessary for the reactions to occur decrease down the group. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride, Li_3N.

(iii) ***Reactivity towards hydrogen.*** The alkali metals react with hydrogen at about 673K (lithium at 1073 K) to form the hydrides, of the formula MH. All the alkali metal hydrides are ionic solids with high melting points. They also react with proton donors such as alcohols, gaseous ammonia and alkynes.

(iv) ***Reactivity towards halogens.*** The alkali metals react directly with halogens to form ionic halides of general formula, MX.

(v) ***Reducing property and E^o values.*** From the E^o values (Table 12.1) it can be seen that the alkali metals are strong reducing agents, lithium being the most and sodium the least powerful. This can be well understood when it is realized that the standard electrode potential (E^0) which measures the reducing power represents here the overall change from M(s) to M^+(aq). Thus the E^0 value depends on the three parameters, i.e. sublimation, ionization and hydration enthalpies. With the small size of its ion lithium has the highest hydration enthalpy which accounts for its high negative E^0 value and its reducing power.

(vi) ***Solutions of the alkali metals in liquid ammonia.*** The alkali metals dissolve in liquid ammonia, the solubility may be as high as 5M. The solutions are coloured and metastable. The dilute solutions are blue but the colour changes to bronze with increasing concentration. The blue colour is attributed to the presence of solvated electrons; the reaction may be represented as

$$M + (x + y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

In concentrated solutions, the ammoniated metal ions are bound by the free unpaired electrons which have been described as 'expanded metals'. The blue solutions are paramagnetic, whereas the bronze-coloured solutions are diamagnetic. The solutions are themselves unstable with respect to amide formation

$$M^+(am) + e^-(am) + NH_3(1) \rightarrow MNH_2(am) + \tfrac{1}{2}H_2(g)$$

$$Na^+(am) + e^-(am) + NH_3(1) \rightarrow NaNH_2(am) + \tfrac{1}{2}H_2(g)$$

However, under anhydrous conditions and in the absence of catalytic impurities such as transition metal ions, solutions can be stored for several days.

12.1.4 General Characteristics of the Compounds of the Alkali Metals

All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are considered here.

(a) Oxides and hydroxides. On combustion in excess of air, lithium forms mainly the oxide, Li_2O (plus some peroxide Li_2O_2), sodium forms the peroxide, Na_2O_2 (plus some Na_2O) whilst potassium, rubidium and caesium form the superoxides, MO_2. Under appropriate conditions pure compounds M_2O, M_2O_2 and MO_2 may be prepared. The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilization of large anions by larger cations through lattice energy effects. These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions:

$$M_2O + H_2O \rightarrow 2M^+ + 2OH^-$$

$$M_2O_2 + H_2O \rightarrow 2M^+ + 2OH^- + \frac{1}{2}O_2$$

$$2MO_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange coloured. The superoxides are also paramagnetic (cf. O_2). Sodium peroxide is widely used as an oxidizing agent in inorganic chemistry.

The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat. Numerous hydrates have been prepared from aqueous solutions of the heavier alkali metal hydroxides, e.g. $NaOH.nH_2O$ (where n = 1,2,3,4,5 and 7) but little is known about their structures.

(b) **Halides.** The alkali metal halides, MX, (where M is an alkali metal and X is a halogen)are all high-melting, colourless crystalline solids which can be conveniently prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). All of these halides have high negative enthalpies of formation; the $\Delta_f H^\ominus$ values for fluorides become less negative as we go down the group, whilst the reverse is true for $\Delta_f H^\ominus$ for chlorides, bromides and iodides. For a given metal $\Delta_f H^\ominus$ always becomes less negative from the fluoride to the iodide (Unit 5)

Trends in many properties of alkali metal halides have been much studied. The melting points and boiling points always follow the trend fluoride>chloride>bromide >iodide. All these halides are soluble in water. The low solubility of LiF is due to its high lattice energy whereas the low solubility of CsI is due to smaller hydration energy of its two ions. In solubilities, lithium salts resemble those of Mg^{2+} salts. Other halides of lithium are soluble in ethanol, acetone and ethyl acetate; LiCl is soluble in pyridine. While dealing with the solubilities of these halides, any generalization may be explained in terms of Born Haber cycle (Unit 6). A delicate balance between lattice enthalpy and hydration enthalpies determines the outcome. All this requires too detailed a treatment to be given here.

(c) **Salts of oxo-acids.** Since the alkali metals are the most electropositive metals they form salts with all the oxoacids. They are generally soluble in water and thermally stable. Their carbonates (M_2CO_3) and in most cases the bicarbonates ($MHCO_3$) also are highly stable to heat. As the electropositive character increases down the group, the stability of the carbonates and bicarbonates increases. Lithium is unusual in so far as its carbonate is not so stable to heat and its bicarbonate does not exist as a solid.

Example 12.1

Arrange the following in order of the increasing covalent character MCl, MBr, MF, MI (where M = alkali metal)

Solution

M F < M Cl < M Br < M I; with increasing size of anion covalent character increases, hence the order.

12.2 ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behaviour of lithium is mainly due to the exceptionally small size of its atom and ion, Li^+ (Table 12.1). Its polarizing power (i.e.charge/radius ratio) is the greatest of all the alkali metal ions. This results in increased covalent character of lithium compounds which is responsible for their solubility in organic solvents. The main points of difference between lithium and the rest of the alkali metals and the points of similarity between lithium and magnesium are given below.

12.2.1 Points of Difference between Lithium and Other Alkali Metals

(i) Lithium is much harder, its m.p.and b.p. are higher than the other alkali metals.

(ii) Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide Li_2O, and the nitride, Li_3N unlike other alkali metals.

(iii) LiCl is deliquescent and crystallizyes as a hydrate, $LiCl.2H_2O$, whereas other alkali metal chlorides do not form hydrates. Lithium bicarbonate is not obtained in the solid form while all other elements of this group form solid bicarbonates.

Lithium unlike other alkali metals forms no acetylide on reaction with ethyne.

(iv) Lithium nitrate when heated gives lithium oxide Li_2O. whereas other alkali metal nitrates decompose to give the corresponding nitrite.

$$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$
$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

(v) LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

Example 12.2

What makes lithium to show properties uncommon to the rest of the alkali metals?

Solution

Exceptionally small size of lithium atom and lithium ion and the high charge/radius ratio of the ion are responsible for such properties.

12.2.2 Points of Similarities between Lithium and Magnesium

These similarities are mainly due to the similarity in sizes of their ions, Li^+ = 76 pm, Mg^{2+} = 72 pm). The main points of similarity are:

(i) Both lithium and magnesium are harder and lighter than other elements in the respective groups.

(ii) Lithium and magnesium react slowly with cold water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride by direct combination with nitrogen, Li_3N and Mg_3N_2.

(iii) The oxides, Li_2O and MgO do not combine with excess oxygen to give a peroxide or a superoxide.

(iv) The carbonates of lithium and magnesium decompose easily on heating to form the oxide and CO_2. Solid bicarbonates are not formed by lithium and magnesium.

(v) Both LiCl and $MgCl_2$ are soluble in ethanol.

(vi) Both lithium perchlorate and magnesium perchlorate are extremely soluble in alcohol.

(vii) Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl.2H_2O$ and $MgCl_2.8H_2O$.

Example 12.3

When is a cation highly polarising? Which alkali metal ion has the highest polarising power?

Solution

A cation is highly polarising if its charge/radius ratio is high. Li^+ ion has the highest polarising power among the alkali metals ions.

12.3 THE METALS

The highly electropositive nature of these elements can be seen from the values of their reduction potentials. (Table 12.1) These values indicate that the reduction of their compounds to produce metals is difficult and requires electrolytic processes.

12.3.1 Lithium

Extraction. The important minerals of lithium include *spodumene*, $LiAlSi_2O_6$; *lepidolite*, $(Li,Na,K)_2Al_2(SiO_3)_3$ $F(OH)$ and *amblygonite*, $LiAl(PO_4)F$. The extraction of lithium involves two steps:

(i) Preparation of lithium chloride from the minerals

(ii) Electrolysis of lithium chloride.

(i) The ore is first heated to about 1373 K to convert it into more friable form, which is then washed with sulphuric acid at 523K and is leached with water to give lithium sulphate, $Li_2SO_4.H_2O$. Successive treatment with sodium carbonate and hydrochloric acid gives, first Li_2CO_3 and finally lithium chloride, LiCl. Alternatively lithium chloride can be obtained by calcining the washed ore with $CaCO_3$ at 1273K followed by leaching with water to give LiOH and then treatment with HCl.

(ii) Electrolysis of lithium chloride. The electrolyte consists of a fused mixture of 55% LiCl and 45% KCl at 723 K. On electrolysis, the molten lithium containing about one per cent potassium is collected (Fig.12.1).

Properties and Uses

Lithium is a soft silvery-white metal. It is harder than sodium but softer than lead. General properties of lithium are given in Table 12.1. It is the smallest element in the group and has the highest ionization enthalpy, melting point, and heat of atomization. Lithium has the lowest

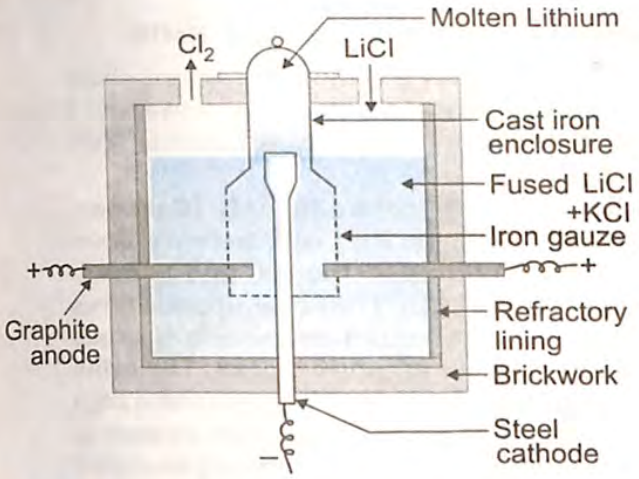


Fig.12.1 *Production of lithium by Electrolysis*
Lithium is also obtained by the electrolysis of concentrated solution of lithium chloride in pyridine, etnanol or acetone.
Current world production of Li metal is about 1000 tonnes annually.

density of any solid at room temperature.

Lithium and its compounds have found variety of uses in recent times. The metal is used as deoxidizer, as an alloying metal, specially with lead to give toughened bearings, and with aluminium to give high strength aluminium alloys for aircraft construction. Its alloy (14% Li) with magnesium is extremely tough and corrosion-resistant which is used for armour plate and aerospace components.

12.3.2 Sodium

Extraction: Enormous quantities of sodium chloride occur as rock-salt deposits and in sea water. Other compounds of sodium found in nature include sodium carbonate, Na_2CO_3 . double sulphate with Ca, borate as borax and complex silicates.

Sodium is extracted by electrolysis of a fused mixture of sodium chloride (40%) and calcium chloride (60%) at 1123 K, in Downs Cell. Metallic sodium and calcium are liberated at the cylindrical steel cathode and rise through a cooled collecting pipe which allows calcium to solidify and fall back into the melt. Molten sodium is taken out of the cell (Fig. 12.2).

Properties and Uses

Physical properties of sodium have been listed in Table 12.1 along with other alkali metals. Other properties of sodium are essentially those as have been described under general characteristics of the alkali metals.

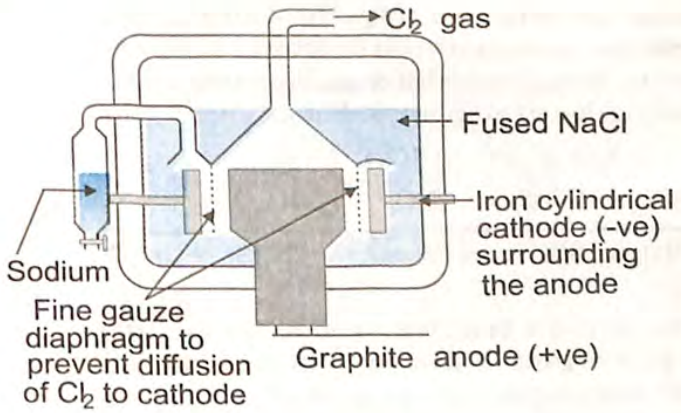

Cl_2 gas
Fused NaCl
Iron cylindrical cathode (-ve) surrounding the anode
Sodium
Fine gauze diaphragm to prevent diffusion of Cl_2 to cathode
Graphite anode (+ve)

Fig.12.2 *Downs Cell*

Industrial uses of sodium metal reflects its strong reducing power. About 60% of world production of sodium is used to make tetraethyl lead, Et_4Pb for gasoline antiknocks. Sodium amalgam is another form in which sodium is widely used as a reducing agent. Sodium metal is also used as a starting material in the preparation of sodium compounds such as sodium peroxide, amide and sodium cyanide. It is also used in dye industry. Liquid sodium is used in nuclear reactors as a medium for heat exchange.

12.3.3 Some Important Compounds of Sodium

Industrially important compounds of sodium include sodium peroxide, sodium hydroxide and sodium carbonate. The large scale production of these compounds and their uses are described below.

Sodium Peroxide, Na_2O_2

Sodium peroxide is manufactured by heating sodium metal on aluminium trays in air (free from CO_2)

$$2Na + O_2(air) \rightarrow Na_2O_2$$

When pure it is clourless, and the faint yellow colour of the usual product arises from the presence of a small amount of NaO_2.When it is exposed, it comes in contact with moist air and turns white due to formation of NaOH and Na_2CO_3. Thus

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

Sodium peroxide is a powerful oxidizing agent and oxidizes chromium (III) hydroxide to sodium chromate, manganese (II) to sodium manganate and sulphides to sulphates. For example

$$[\ O_2^{2-} + 2H_2O + 2e^- \rightarrow 4OH^-\ ] \times 3$$

$$[\ Cr(OH)_3 + 5OH^- \rightarrow CrO_4^{2-} + 4H_2O + 3e^-\ ] \times 2$$

$$2Cr(OH)_3 + 3O_2^{2-} \rightarrow 2CrO_4^{2-} + 2OH^- + 2H_2O$$

Uses

Sodium peroxide is widely used as an oxidizing agent in inorganic chemistry; its reaction with organic compounds are dangerously violent.

(i) Since it readily combines with carbon dioxide yielding sodium carbonate and oxygen, it may be used for the purification of air in confined spaces such as submarines.

(ii) It is also used as a bleaching agent because of its oxidizing property

(iii) Sodium peroxide is used in the manufacture of dyes, and many other chemicals such as benzoyl peroxide, sodium perborate, etc.

Example 12.4

Why is it that on being heated in excess supply of air K, Rb and Cs form super oxides in preference to oxides and peroxides?

Solution

K^+, Rb^+ and Cs^+ are large cations and super oxide ion, O_2^- is also large. As a general rule the larger cations stabilize larger anions. Hence super oxides are formed by these metals.

Sodium Hydroxide (caustic soda), NaOH

Sodium hydroxide is the most important alkali and is made commercially by the electrolysis of a saturated solution of sodium chloride. Two kinds of cell are used.

(a) **The mercury cathode cell (Castner-Kellner cell)**: In this cell mercury flows along the bottom of the cell and is made cathode (Fig. 12.3). The brine solution flows in the same direction and anode consists of a number of graphite blocks. The brine electrolyzes and since, hydrogen has a high overvoltage at mercury cathode, sodium is preferentially discharged forming amalgam with mercury.

The sodium amalgam flows out and is reacted with water to give NaOH

$$2NaHg + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$$

The mercury is re-circulated to the cell. Hydrogen and chlorine are the two important by-products (see Unit 11)

(b) **Diaphragm cell:** In this type of cell (Fig. 12.4) alkali and chlorine are kept separate by use of a diaphragm and on contact with a negative wire gauze, electrolysis begins. Chlorine is liberated at graphite anode and sodium hydroxide is formed at the outside edges of the cathode.

(c) **Using Nafion Membrane Cell**: The natural brine (NaCl) is now electrolysed in a membrane cell in which the anolyte and the catholyte are separated by a NAFION membrane. Nafion is a copolymer of tetrafluoromethylene and pentafluorosulphonyl ethoxyether. The copolymer is supported by a Teflon mesh.

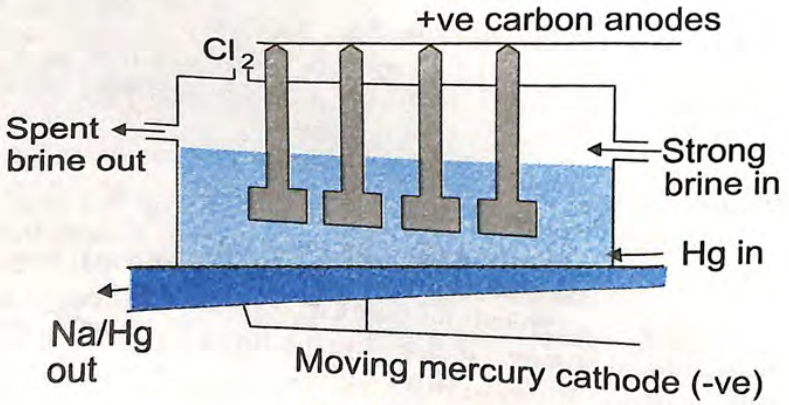


Fig. 12.3 *The Castner- Kellner Cell*

At the anode (+)

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

At the cathode (-)

$$Na^+ + e^- \longrightarrow Na$$

$$Na + Hg \longrightarrow NaHg$$

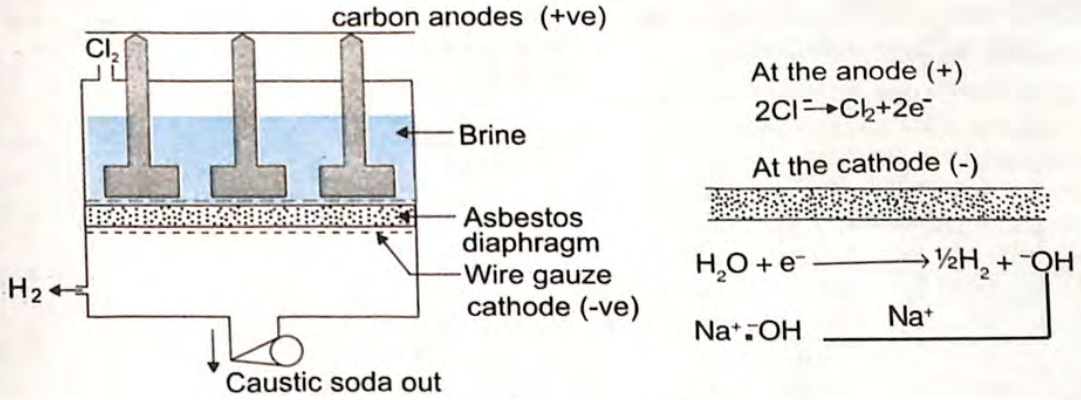


Fig.12.4 A Diaphragm Cell

$$2NaCl\ (aq) + H_2O(l) \xrightarrow{\text{Electrolysis}} 2NaOH(aq) + H_2\ (g) + Cl_2\ (g)$$

At present India produces nearly 1.35 million tonnes of caustic soda annually. Presently the method makes use of Nafion membrane in place of diaphragm.

Sodium hydroxide is a deliquescent solid and absorbs moisture and carbon dioxide, finally setting to a solid hydrated carbonate. An aqueous solution contains large concentration of hydroxyl ion (OH^-) and generally precipitates insoluble metal hydroxides from solutions containing metallic cations. The hydroxides of aluminium, zinc, lead and tin, however, dissolve in excess of sodium hydroxide giving clear solution which can also be obtained when these metals are acted upon by the concentrated solution of sodium hydroxide. For example, some reactions are as under.

$$Zn(OH)_2 + 2OH^- \rightarrow \underset{\text{Zincate ion}}{[Zn(OH)_4]^{2-}}$$

$$Al(OH)_3 + 3OH^- \rightarrow \underset{\text{Aluminate ion}}{[Al(OH)_6]^{3-}}$$

$$Zn + 2OH^- + 2H_2O \rightarrow [Zn(OH)_4]^{2-} + H_2$$

$$2Al + 6OH^- + 6H_2O \rightarrow 2[Al(OH)_6]^{3-} + 3H_2$$

Uses

Sodium hydroxide finds many important uses:

(i) in soap industry
(ii) in paper industry
(iii) in textile industry
(iv) for the preparation of pure fats and oils
(v) for preparation of artificial silk
(vi) in petroleum industry
(vii) for the absorbing of acidic gases
(viii) as a reagent in laboratories

Sodium Carbonate, $Na_2CO_3.10H_2O$

Manufacture (Solvay Process): In principle the reaction involved in the manufacture of sodium carbonate is, that between sodium chloride and calcium carbonate, i.e.

$$2NaCl + CaCO_3 \longrightarrow Na_2CO_3 + CaCl_2$$

However, this reaction is reversible and creates other problems in the system and, therefore, other chemicals are required to get the desired product. The raw materials include sodium chloride, calcium carbonate, ammonia and fuel. The calcium carbonate is strongly heated to give quick lime and carbon dioxide:

$$CaCO_3 \longrightarrow CaO + CO_2 \quad (1)$$

The carbon dixide is passed up a large tower with perforated plates down which a concentrated solution of sodium chloride saturated with ammonia (ammoniated brine, Fig.12.5) trickles down. The reactions taking place in the tower can be represented as

$$NH_3 + H_2O \longrightarrow NH_3.H_2O \longrightarrow NH_4^+ + OH^- \quad (2)$$

$$Na^+ + Cl^- + NH_4^+ + OH^- + CO_2 \longrightarrow Na^+ + HCO_3^- + NH_4^+ + Cl^- \quad (3)$$

$$Na^+ + HCO_3^- \longrightarrow NaHCO_3 \text{ (as precipitate)} \quad (4)$$

$$NH_4^+ + Cl^- \longrightarrow NH_4Cl \text{ (in solution)}$$

Sodium hydrogen carbonate (or bicarbonate) which is not very soluble in the presence of NaCl (common ion effect) is filtered and heated to produce sodium carbonate

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \quad (5)$$

The sodium carbonate obtained (5) in this way

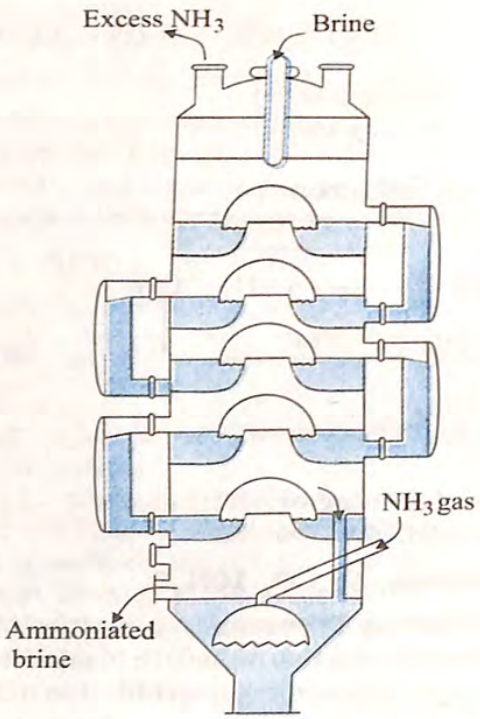


Fig.12.5 *The Ammoniation of brine solution (Solvay process)*

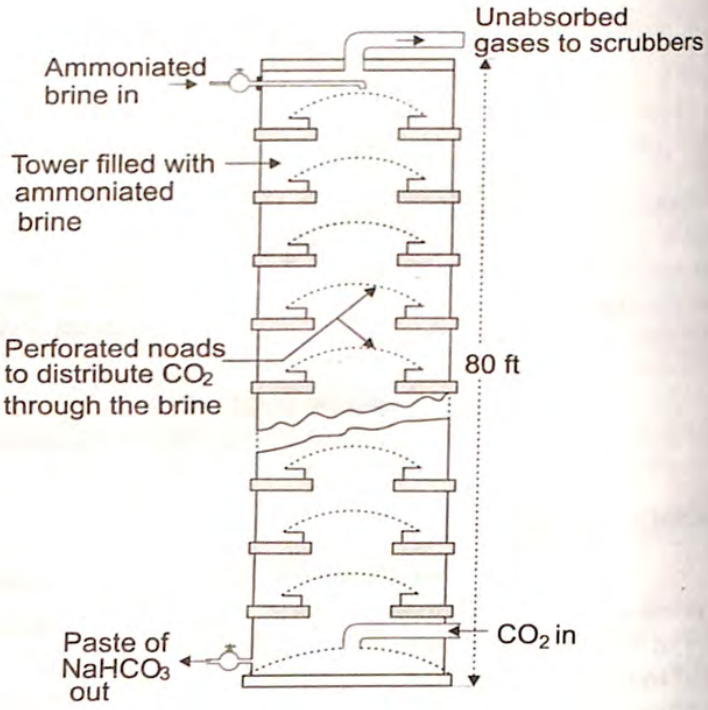

Unabsorbed gases to scrubbers
Ammoniated brine in
Tower filled with ammoniated brine
Perforated noads to distribute CO_2 through the brine
80 ft
CO_2 in
Paste of $NaHCO_3$ out

Fig.12.6 *Carbonating tower (Solvay process)*

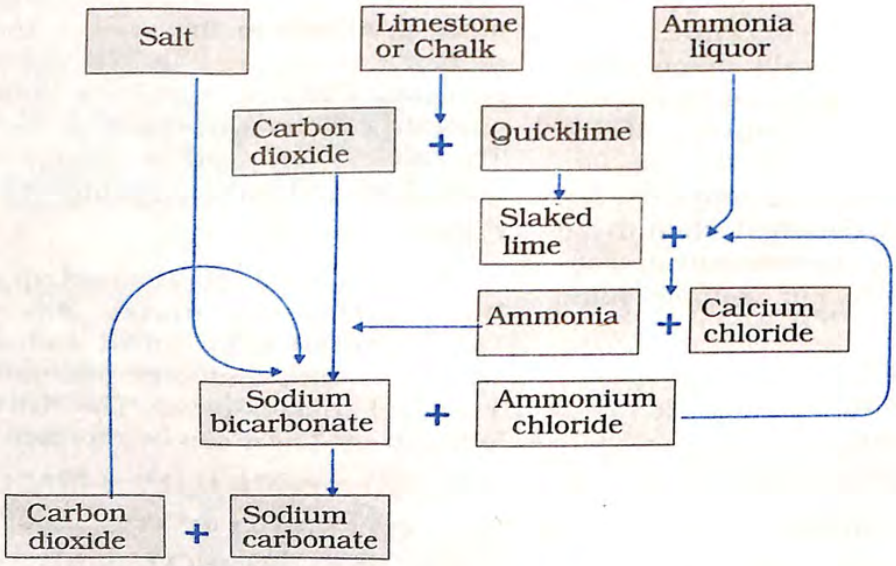


Fig.12.7 *Solvay process (schematic)*

is contaminated with ammonium salts. It is purified by blowing carbon dioxide through its aqueous solution. The sodium hydrogen carbonate formed in this way is filtered and heated to give pure sodium carbonate. Recrystallization from water produces soda, $Na_2CO_3.10H_2O$.

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3 \quad (6)$$

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \quad (7)$$

The Solvay process is very economical because, except for NaCl and $CaCO_3$, other raw materials used in the process are not consumed. Thus:

(i) quick-lime and ammonia formed in

reaction (I) and (3) are reacted to produce ammonia, so that apart from making up of small losses, no additional ammonia is required.

(ii) carbon dioxide formed in reaction (5) and (7) is reintroduced into the tower

(iii) NaCl and $CaCO_3$ are cheap materials. Calcium chloride is obtained as a bye-product which finds no large scale industrial applications.

(***Note***: Potassium carbonate cannot be prepared by Solvay process as the solubility of $KHCO_3$ is fairly large as compared to $NaHCO_3$.)

In India it is manufactured at Tata Chemical Works at Mithapur in Gujrat. India produces nearly 1.54 million tonnes of soda ash (Na_2CO_3) annually at present.

Uses of Sodium Carbonate

It is one of the most important heavy chemicals in industry. Many important uses include:

(i) glass and soap industry
(ii) paper making and textile manufacture
(iii) water softening, laundering and cleaning
(iv) paint and dye stuffs
(v) metal refining
(vi) production of sodium compounds such as borax, caustic soda, sodium phosphate, etc.

Example 12.5

What happens when KO_2 reacts with water? Write the balanced chemical equation for this reaction.

Solution

$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$

(i.e. $2O_2^- + 2H_2O \longrightarrow 2OH^- + H_2O_2 + O_2$)

An alkaline solution containing hydrogen peroxide with the evolution of oxygen is produced.

Example 12.6

Predict giving reason the outcome of the reaction :

$LiI + KF \longrightarrow$ - - - - - - - -

Solution

$LiI + KF \longrightarrow LiF + KI$; larger cation stabilizes larger anion.

12.4 GENERAL CHARACTERISTICS OF THE ALKALINE EARTH METALS

Group 2 of the periodic table comprises the elements beryllium, magnesium, calcium, strontium, barium and radium. These (except beryllium) are known as the alkaline earth metals (see Introduction to this Unit).

The general relationships throughout the group are similar to those in Group1. The first element beryllium shows 'diagonal relationship' to aluminium. Table 12.2 gives some atomic and physical properties of the alkaline earth metals. Let us first consider the general characteristics of these elements.

12.4.1 Atomic Properties

(i) ***Electronic configuration***: A comparison with electronic configurations of the alkali metals shows that these metals with an increased nuclear charge of one unit have ns^2 configuration over and above the noble gas configuration in the respective periods. The number of valence electrons in these metals is, therefore, 2 (Table 12.2).

(ii) ***Atomic and ionic sizes:*** The atomic and ionic radii of the alkaline earth metals are smaller than those of the alkali metals in the corresponding periods. This is due to the increased nuclear charge in these elements.

(iii) ***Ionization Enthalpies*** : The first ionization enthalpies of the alkaline earth metals are higher than those of Group 1 metals. It is interesting to note that the second ionization enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metals (see Unit 4).

12.4.2 Physical Properties

(i) ***Physical appearance***: These metals in general are silvery white, lustrous and relatively soft, but harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish.

(ii) ***Melting and boiling points***: The fairly higher melting and boiling points of the alkaline earth metals compared to those of the corresponding alkali metals and attributed to their smaller atomic sizes and presence of two valence electrons. The trend is however, not systematic.

Table 12.2 Atomic and Physical Properties of the Alkaline Earth Metals

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Srontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Electron configuration	[He]$2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$
Ionization enthalpy (I)/kJ mol^{-1}	899	737	590	549	503	509
Ionization enthalpy (II)/kJ mol^{-1}	1757	1450	1145	1064	965	979
Metallic radius/pm	112	160	197	215	222	-
Ionic radius(M^{2+})/pm	31	72	100	118	135	148
m.p. /K	1562	924	1124	1062	1002	973
b.p. /K	2745	1363	1767	1655	2078	(1973)
Density /g cm^{-3}	1.84	1.74	1.55	2.63	3.59	(5.5)
E^0/V for (M^{2+}/M)	-1.97	-2.36	-2.84	-2.89	-2.92	-2.92
Occurrence in Lithosphere	2*	2.76**	4.6**	384*	390*	10^{-10}**

* ppm (part per million) ** percentage by weight

(iii) Electrical and thermal conductivities: These properties are characteristic of typical metals.

(iv) Flame colour: Calcium, strontium and barium impart characteristic brick red, crimson and apple green colours to the flame respectively. In flame the electrons are excited to higher energy levels and when they drop back to the original state, energy is emitted in the form of visible light. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence, these elements do not impart any colour to the flame. The flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis .

12.4.3 Chemical Reactivity

(i) Towards air and water: The alkaline earth metals are reactive metals though less reactive than the alkali metals. Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of a surface film of oxide. Beryllium does not react with water or steam even at red heat and does not oxidize in air below 873K. Though powdered beryllium burns brilliantly on ignition to give BeO and Be_3N_2. Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and Mg_3N_2. Calcium, strontium and barium are readily attacked by air to form the oxide and nitride. They also react with water with increasing vigour even in cold.

(ii) Towards the halogens: The alkaline earth metals react with halogens at elevated temperatures to form the halides of the type, MX_2.

(iii) Action of acids: The alkaline earth metals readily react with acids liberating hydrogen.

(iv) With ammonia: Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions from which ammoniates $[M(NH_3)_6]^{2+}$ can be recovered.

(v) ***Reducing power and E^0 values***:The near constancy of the E^0 (M^{2+}/M) values for Group 2 metals (Table 12.2) are somewhat similar to those for Group1 metals. Therefore, these metals are electropositive and are strong reducing agents. The particularly less negative value for Be arises from the large hydration energy associated with the small size of Be^{2+} and the relatively large value of the enthalpy of atomization of the metal. The magnesium cation is more easily reduced than the cations of the heavier members of the group because its smaller size leads to a relatively large negative value for its hydration enthalpy.

12.4.4 General Characteristics of Compounds of the Alkaline Earth Metals

The tendency to form dipositive ions by these metals can be explained in terms of the parameters used in Born Haber's cycle (Unit 6). The formation of MX or MX_3 is precluded on these considerations. For example the enthalpy of hypothetical MgCl is -125 kJ mol^{-1} and the corresponding value for $MgCl_2$ is -642kJ mol^{-1}. Thus the enthalpy of the disproportionation reaction, $2MgCl \longrightarrow MgCl_2 + Mg$ is -642- 2(-125) =-392 kJ/ mol. This shows that any synthetic route to get MX in case of the alkaline earth metals will result in the formation of MX_2. Hence, they are uniformally dipositive in their compounds.

With the increased nuclear charge and smaller size, the alkaline earth metals form compounds which are less ionic than the corresponding compounds of the alkali metals. The oxides and salts of the light and small sized members such as Be and Mg are more covalent than those formed by the heavier and larger sized members (Ca, Sr, Ba). A general survey of some of their compounds is presented below.

(a) ***Oxides and hydroxides***: All of them form oxides of the formula MO (M= an alkaline earth metal) which except for BeO have rock- salt structure. The bond in BeO is essentially covalent. The enthalpies of formation of these oxides are quite high and consequently they are very stable.

Metal oxide	BeO	MgO	CaO	SrO	BaO
$\Delta_f H^\ominus$ (kJ mol^{-1})	–550	–601	–635	–590	–545

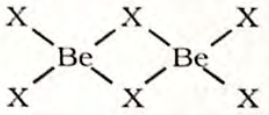
All these oxides except BeO react with water to form sparingly soluble hydroxides

$$MO + H_2O \longrightarrow M(OH)_2$$

The solubility, thermal stability and the basic character of these hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$. Beryllium hydroxide, $Be(OH)_2$ like BeO reacts with acids as well as with alkalies and is thus amphoteric

$$Be(OH)_2 + 2OH \longrightarrow [Be(OH)_4]^{2-}$$
(beryllate ion)

(b) ***Halides***: Except for beryllium halides all other halides of these metals are ionic in nature. Beryllium halides are essentially covalent and are soluble in organic solvents. The BeX_2 molecules exist only in gas phase but in condensed phases it exists as a polymer in which beryllium is 4 - coordinated as shown below:



(where X = a halogen)

Of the other halides only $MgBr_2$ and MgI_2 are soluble in organic solvents. The tendency to form halide hydrates gradually decreases, (for example.$MgCl_2.8H_2O$, $CaCl_2.6H_2O$, $SrCl_2.6H_2O$, and $BaCl_2.2H_2O$) down the group. The hydrated chlorides, bromides and iodides of calcium, strontium and barium can be dehydrated by heating but those of magnesium and beryllium suffer hydrolysis.

The fluorides of the alkaline earth metals are sparingly soluble in water, the solubility increases slightly with increase in cation size. Calcium fluoride (CaF_2) is by far the most important of all the fluorides of the alkaline earth metals since CaF_2 (fluorospar) is the only large scale source of fluorine.

(c) ***Salts of oxoacids***: As in Section (12.1.4) dealing with the alkali metal salts of oxoacids, we shall consider only a few such salts which are of some importance.

Carbonates. Most beryllium salts of strong oxo-acids crystallize as soluble hydrates. Beyllium carbonate is prone to hydrolysis and can be precipitated only in an

atmosphere of carbon dioxide. The carbonates of magnesium and the other alkaline earth metals are all sparingly soluble in water; their thermal stability increases with increasing cationic size. All these carbonates are more soluble in the presence of carbon dioxide in water owing to the formation of hydrogen carbonate ion (HCO_3-) but bicarbonates have not been isolated in pure state. Calcium carbonate finds use in Solvay process for the manufacture of sodium carbonate, in glass making and in cement manufacture (see Section 12.7.6).

Sulphates: The sulphates of the alkaline earth metals are all white solids and stable to heat. The sulphates, $BeSO_4$ and $MgSO_4$ are readily soluble; the solubility decreases from $CaSO_4$ to $BaSO_4$. Beryllium, magnesium and calcium sulphates crystallize in hydrated form, $BeSO_4.4H_2O$; $MgSO_4.7H_2O$; $CaSO_4.2H_2O$. The sulphates of strontium and barium crystallize without water.The greater hydration energies of Be^{2+} and Mg^{2+} ions overcome the lattice energy factor and, therefore, their sulphates are soluble.

Oxalates: The oxalates of Ca, Sr, Ba are sparingly soluble and solubility increases from calcium to barium. Beryllium oxalate is highly soluble and magnesium oxalate falls in line with the rest.

Nitrates: The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallizes with six molecules of water. Barium nitrate crystallizes as the anhydrous salt. All of them decompose on heating, giving the oxide.

$$2M(NO_3)_2 \longrightarrow 2MO + 4NO_2 + O_2$$

(M=Be, Mg, Ca, Sr or Ba)

Strontium and barium nitrates are used in pyrotechnics for giving red and green flames. From all the above general characteristics of the elements of Group 2, it appears that calcium, strontium and barium form a closely related distinct group where physical and chemical properties change systematically with increasing atomic size. Thus Ca, Sr and Ba are highly electropositive, have high negative E^o values, and exhibit systematic trends in solubility of their oxo-salts.

Example 12.7

Name one reagent or one operation to distinguish between

(i) $BeSO_4$ and $BaSO_4$

(ii) $Be(OH)_2$ and $Ba(OH)_2$

Solution

(i) $BeSO_4$ is soluble in water while $BaSO_4$ is not

(ii) $Be(OH)_2$ dissolves in NaOH while $Ba(OH)_2$ is insoluble

12.5 ANOMALOUS BEHAVIOUR OF BERYLLIUM

The anomalous behaviour of beryllium is reflected in the following:

(i) Beryllium has exceptionally small atomic and ionic sizes (Table 12.2) and, thus, does not compare with other members of the group. Because of high ionization energy and small atomic size it forms compounds which are largely covalent and its salts are easily hydrolyzed.

(ii) Beryllium does not exhibit coordination number more than four as in its valence shell (n=2) there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of some *d*-orbitals in addition to *s*- and *p* orbitals.

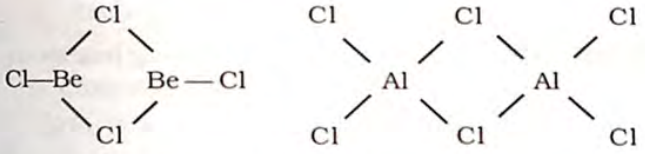
(iii) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in this group are amphoteric in nature.

Diagonal similarity between beryllium and aluminium: In many of its properties, beryllium resembles aluminium. Thus:

(i) The two elements have same electronegativity (Be 1.5; Al 1.5) and their charge/radius ratios (~0.064 and ~0.060 respectively) are very similar indicating similar field strengths.

(ii) Both metals are fairly resistant to the action of acids due to a protective film of oxide on the surface. Both metals are acted upon by strong alkalies to form soluble complexes, beryllates $[Be(OH)_4]^{2-}$ and aluminates, $[Al(OH)_4]^-$.

(iii) The chlorides of both beryllium and aluminium have bridged chloride structures in vapour phase



(iv) Salts of these metals form hydrated ions, e.g $[Be(OH_2)_4]^{2+}$ and $[Al(OH_2)_6]^{3+}$ in aqueous solutions. Because of the similarity of charge/radius ratios beryllium and aluminium ions have strong tendency to form complexes. For example beryllium forms tetrahedral complexes such as BeF_4^{2-} and $[Be(C_2O_4)_2]^{2-}$ and aluminium forms octahedral complexes like AlF_6^{3-} and $[Al(C_2O_4)_3]^{3-}$.

Next we shall discuss the extraction and uses of **magnesium**, the most important metal of the group in many respects and some compounds of alkaline earth metals which are of industrial importance.

Example 12.8

Why does beryllium show similarities with Al ?

Solution

Because of their similarity in charge/radius ratios (Be^{2+}, 2/31=0.064; Al^{3+}, 3/50=0.060).

12.6 MAGNESIUM METAL

Magnesium occurs as *magnesite* $MgCO_3$, *dolomite*, $CaMg(CO_3)_2$, *epsomite*, $MgSO_4.7H_2O$ and *carnallite*, $K_2MgCl_4.6H_2O$ and *langbeinite*, $K_2Mg_2(SO_4)_3$ deposits. The chloride and sulphate of magnesium occur in sea water from which it is being extracted on an increasing scale. India has a good reserve (~250 million tonnes of magnesite ore, mostly in U.P. Tamil Nadu and Rajasthan.

12.6.1 Extraction

(a) From Magnesite or Dolomite: The ore is first Calcined to form the Oxide

$$MgCO_3 \longrightarrow MgO + CO_2$$

$$CaCO_3.MgCO_3 \longrightarrow CaO.MgO + 2CO_2$$

The metal is obtained from the oxide or the mixed oxides as follows.

(i) From MgO. The oxide is mixed with carbon and heated in a current of chlorine gas

$$MgO + C + Cl_2 \longrightarrow MgCl_2 + CO$$

The chloride thus obtained is subjected to electrolysis (see below).

(ii) The mixed oxides (CaO.MgO) obtained from calcination of dolomite ($CaCO_3MgCO_3$)are reduced by ferrosilicon under reduced pressure above 1273K.

$$2CaO.MgO + FeSi \longrightarrow 2Mg + Fe + Ca_2SiO_4$$

(b) From carnallite: The ore is dehydrated in a current of hydrogen chloride and the mixture of fused chloride is electrolysed (see below).

(c) From sea water: Sea water containing magnesium chloride is concentrated under the sun and is treated with calcium hydroxide, $Ca(OH)_2$. Magnesium hydroxide is thus precipitated, filtered and heated to give the oxide. The oxide so obtained is treated as in (a) (i) above and then electrolysed.

Electrolysis of magnesium chloride: Magnesium chloride obtained by any of the above methods (a) (i), (b) or (c) is fused and mixed with additional mixture of sodium chloride and calcium chloride in the temperature range of 973-1023K. The molten mixture is electrolysed. Magnesium is liberated at the cathode and chlorine is evolved at the anode :

At Cathode: $Mg^{2+} + 2e^- \longrightarrow Mg$

At Anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$

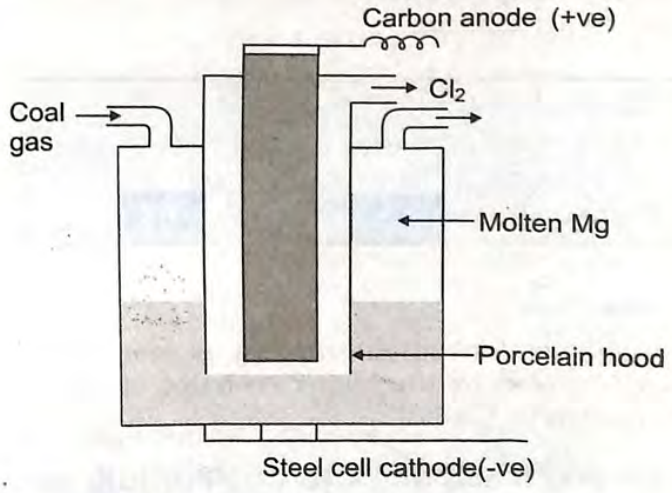


Fig 12.8 *Electrolysis of magnesium chloride*

A stream of coal gas is blown through the cell to prevent oxidation of magnesium metal (Fig. 12.8). Magnesium metal is obtained in liquid state which is further distilled to give pure magnesium.

12.6.2 Properties and Uses

Magnesium like beryllium is a greyish white metal. Its atomic and physical properties are listed along with others in Table12.2. It appears to be unreactive to oxygen and water due to the formation of a surface film of the oxide. Magnesium amalgam liberates hydrogen from water. The metal decomposes steam and readily reacts with acids including nitric acid. Magnesium burns in air to give the oxide, MgO and the nitride, Mg_3N_2. It also reacts with most of the non-metals. Alkyl and aryl halides react with magnesium to give Grignard's reagents.

Magnesium is the lightest constructional metal in industry having a density less than two thirds of aluminium. It is an important alloying metal. Some of the magnesium alloys contain more than 90% Mg together with 2-9% Al and 1% Zn. These alloys are used in automobile engines and in aeroplanes. Up to 5% Mg is added to most commercial aluminium alloys(e.g. duralumin, magnalium) to improve its mechanical properties, weldability and resistance to corrosion. Magnesium is also used for cathodic protection of other metals, as an oxygen scavenger, as a reducing agent in the production of certain metals such as Ti, Zr and Hf, and the preparation of Grignard reagent. World production of magnesium exceeds 300,000 tonnes per annum.

Example 12.9

The second ionization enthalpy of calcium is more than that of the first and yet calcium forms $CaCl_2$ not CaCl. Why ?

Solution

The higher ionization enthalpy is more than compensated by the higher enthalpy of lattice formation by Ca^{2+}.

12.7 SOME IMPORTANT COMPOUNDS OF THE ALKALINE EARTH METALS

Important compounds of the alkaline earth metals include calcium oxide, calcium hydroxide, plaster of Paris and magnesium suplhate. Some other substances of industrial importance are limestone and cement.

12.7.1 Calcium Oxide (Quicklime), CaO

Preparation. It is produced by heating limestone at about 1273K in lime kilns. The reaction

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

is reversible and proceeds efficiently when carbon dioxide is allowed to escape from the system. It is only above 1100 K that the gas escapes freely and hence a temperature of 1273K is maintained.

Properties

(i) Pure calcium oxide or quicklime is an amorphous white solid of very high melting point, about 2273K.

(ii) It is usually obtained in the form of hard lumps and when heated in oxyhydrogen flame emits a brilliant white light (*lime-light*).

(iii) It readily absorbs moisture and carbon dioxide:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
$$CaO + CO_2 \longrightarrow CaCO_3$$

The reaction with water is highly exothermic

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)(aq)_2 ; \Delta H = -64.5 kJ/mol$$

(iv) Slaking . The addition of limited amount of water disintegrates the lump of lime. The process is known as *slaking* of lime and the product slaked lime. Quicklime slaked with soda gives a solid, sodalime.

(v) It combines with solid acidic oxides at high temperatures

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
$$6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$$

Uses

(i) It is used as a drying agent as such or as sodalime.

(ii) Large quantities of quick-lime are used in the production of slaked lime (for use in the preparation of bleaching powder).

(iii) As a constituent of mortar, it is used on a very large scale in building constructions.

12.7.2 Calcium Hydroxide, (Slaked lime) $Ca(OH)_2$

(i) Slaked lime is produced when water is added to quick-lime.

(ii) It is a white powder, and is sparingly soluble in water. The aqueous solution is known as *lime water* and a suspension of slaked lime in water is known as *milk of lime*.

(iii) When carbon dioxide is passed through lime water it turns milky

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

On passing excess of carbon dioxide, the precipitate dissolves owing to the formation of calcium hydrogen carbonate

$$CaCO_3 + CO_2 + H_2O \longrightarrow \underset{\text{(soluble)}}{Ca(HCO_3)_2}$$

(iv) On heating slaked lime loses water only at temperatures >700K.

(v) Since it is strongly basic it reacts with acids and acidic gases forming salts.

(vi) Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + Ca(ClO)_2 + 2H_2O$$

Uses

Calcium hydroxide finds various uses:

(i) For absorbing acid gases

(ii) For preparing ammonia from ammonium chloride

(iii) In the production of mortar, a building material

(iv) In glass making, tanning industry, for the preparation of bleaching powder, and for purification of sugar

(v) It is also used as a disinfectant.

(vi) As lime water in laboratories.

12.7.3 Plaster of Paris, $CaSO_4.\frac{1}{2}H_2O$

Plaster of Paris is an important commercial substance. It is obtained when gypsum, $CaSO_4.2H_2O$ is heated to 393K

$$2(CaSO_4.2H_2O) \longrightarrow 2CaSO_4.H_2O + 3H_2O$$

Thus it has one molecule of water for every two calcium and two sulphate ions. The heating has to be carefully controlled otherwise anhydrous salt, $CaSO_4$ is produced which has no such property as plaster of Paris (the hemihydrate $CaSO_4.\frac{1}{2}H_2O$).

Plaster of Paris is a white powder which when wetted with one-third of its weight of water sets with expansion into a hard mass of interlocking crystals of gypsum within 5-15 minutes. The addition of common salt accelerates the rate of setting, while a little borax or alum reduces it. When heated above 473K it gives anhydrous $CaSO_4$ which does not set on mixing with water and is termed as 'dead-burnt plaster'.

Uses

Plaster of Paris finds extensive use in surgical bandages, in casting and moulding. It is also employed in dentistry, in ornamental work and for taking casts of statues and busts.

12.7.4 Magnesium Sulphate, $MgSO_4.7H_2O$

Preparation and Properties: Magnesium occurs in earth's crust as minerals *kieserite*, $MgSO_4.2H_2O$ and *epsomite*, $MgSO_4.7H_2O$. It is prepared from these minerals by fractional crystallization. It can also be obtained from minerals *magnesite*, $MgCO_3$ or *dolomite* $CaMg(CO_3)_2$ on treatment with sulphuric acid

$$CaCO_3.MgCO_3 + 2H_2SO_4 \longrightarrow CaSO_4 + MgSO_4 + 2H_2O + 2CO_2$$

The two sulphates can easily be separated by fractional crystallization.

When crystallized from solutions in the temperature range 275-320K, magnesium sulphate corresponds to the formula $MgSO_4.7H_2O$ and is known as Epsom salt. Above 320K lower hydrates are formed and at about 573K all water is lost. On further heating the anhydrous sulphate decomposes to form the oxide.

The correct formulation of the heptahydrate is $[Mg(H_2O)_6]SO_4.H_2O$. The crystals of the heptahydrate are colourless and isomorphous with zinc sulphate , $ZnSO_4.7H_2O$. Magnesium sulphate is deliquescent and readily soluble in water. It forms double salts with alkali metal sulphates. The double salt, $K_2SO_4.MgSO_4.6H_2O$, is sold as a fertilizer in the name of 'potash magnesis'.

Uses

Magnesium sulphate is used

(i) in weighting, sizing and fire-proofing of paper and cloth,

(ii) in the preparation of paints and soaps,

(iii) in dyeing and tanning and

(iv) as a purgative in medicine.

12.7.5 Limestone, $CaCO_3$

Limestone rock is the commonest form of calcium

carbonate, which also occurs as chalk, marble, corals, calcite, aragonite, etc, and (with Mg) as dolomite. Limestone is widely used as a building material and a road aggregate. It is quarried on a vast scale worldwide. It is also a major industrial chemical and is indispensible as the precursor of quick lime (CaO) and slaked lime $Ca(OH)_2$. These chemicals are crucial to large sections of the chemical, metallurgical and construction industries. (See earlier for quick lime and slaked lime).

12.7.6 Portland Cement

The name 'Portland cement' was first used by J. Aspdin in 1824 because when mixed with water and sand the powder hardened into a block that resembled the natural limestone quarried in the Isle of Portland, England. With subsequent experimentation and improvement in technology Portland cement became the most important building material throughout the world (total world production of cement in 1974 was over 700 million tonnes). India is producing nearly 100 million tonnes of cement annually (1999-2000). Portland cement is made by heating a mixture of limestone (or chalk, shells, etc.) with aluminosilicates (derived from sand, clays and shales) in carefully controlled amounts so as to give the approximate composition CaO 70%, SiO_2 20%, Al_2O_3 5%, Fe_2O_3 3%. The raw materials are ground to pass 300-mesh sieves and then heated in a rotary kiln (Fig 12.9) to 1773K to give sintered clinker; this is ground to 325-mesh sieve and mixed with 2-5% gypsum. An average sized kiln can produce 1000-2000 tonnes of cement per day.

The important compounds present in Portland cement are dicalcium silicate (Ca_2SiO_4) 26%, tricalcium silicate (Ca_3SiO_5) 51%, and tricalcium aluminate ($Ca_3Al_2O_6$) 11%.

When mixed with water, the setting of cement takes place. Chemically speaking it is the hydration of the molecules of the constituents and their rearrangement.

The adhesion of other particles to each other and to the embedded aggregates is responsible for the strength of the cement which is due, ultimately, to the formation of Si-O-Si-O bonds.

The purpose of adding gypsum is only to slow down the process of setting of the cement so that it gets sufficiently hardened.

Uses

Cement has become so important that next to iron and steel it can be classed as a commodity of national necessity for any country. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

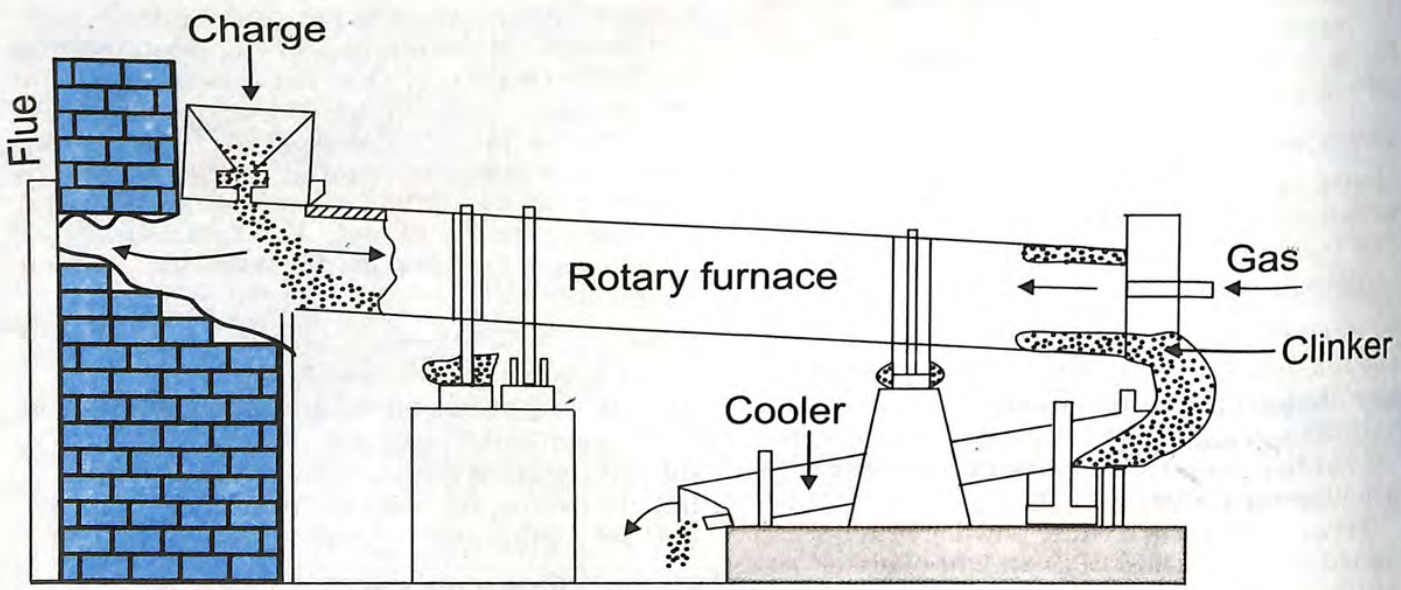


Fig.12.9 Rotary kiln

SUMMARY

The alkali metals present in Group 1 and the alkaline earth metals present in Group 2 constitute the s-block of the periodic table. They are so called because their oxides or hydroxides are alkaline in nature. The alkali metals are characterized by one s-electron and the alkaline earth metals by two s-electrons in the valence shell of their atoms. These are highly reactive metals forming monopositive (M^+) and dipositive (M^{2+}) ions respectively.

There is a regular trend in the physical and chemical properties of the alkali metals with increasing atomic numbers. The atomic and ionic size increase and the ionization enthalpy decreases systematically down the group. Somewhat similar trends are observed among the properties of the alkaline earth metals.

These metals do not occur in the free state in nature. Since they are highly electropositive, they are generally extracted by electrolytic methods.

The alkali metals are silvery white, soft and low melting. They are highly reactive and react with water and with most of the non-metals. The compounds of the alkali metals are predominantly ionic. Their oxides and hydroxides are soluble in water forming strong alkalies. The oxoacid salts of the alkali metals are well known and are easily soluble in water. They also form solid bicarbonates which are, however, relatively less soluble.

Sodium peroxide, sodium hydroxide and sodium carbonate are among the important compounds of the alkali metals. Sodium hydroxide is manufactured by Castner-Kellner process and sodium carbonate by Solvay process.

The chemistry of the alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of the reduced atomic and ionic sizes and increased cationic charges in case of the alkaline earth metals. Their oxides and hydroxides are also strongly basic but less so than the corresponding alkali metal oxides and hydroxides.

Similarly the oxo-salts of the alkaline earth metals are relatively less soluble and thermally less stable than those of the alkali metals.

The first element in each of these groups, lithium in Group 1 and beryllium in Group 2 shows similarities to the second member of the next group. Such similarities are termed as the 'diagonal relationship' in the periodic table. As such these elements are anomalous as far as their group characteristics are concerned.

Some of the compounds of calcium are industrially very important. Notable among them are calcium oxide (lime), calcium carbonate (limestone) and calcium sulphate (Gypsum and Plaster of Paris). Portland cement is an important constructional material. It is manufactured by heating a pulverized mixture of limestone and clay in a rotary kiln. The clinker thus obtained is mixed with some gypsum (2-3%) to give a fine powder of cement. All these substances find variety of uses in different areas.

EXERCISES

12.1 Write three general characteristics of the elements of s-block of the periodic table which distinguish them from the elements of the other blocks.

12.2 The alkali metals follow the noble gases in their atomic structure. What properties of these metals can be predicted from this information?

12.3 What happens when
(i) sodium metal is dropped in water?
(ii) sodium metal is heated in free supply of air?
(iii) sodium peroxide dissolves in water?

12.4 Name the alkali metals which form superoxides when heated in excess of air.

12.5 Name the metal which floats on water without any apparent reaction with it.

12.6 List three properties of lithium in which it differs from the rest of the alkali metals.

12.7 Name the chief factor responsible for the anomalous behaviour of lithium.

12.8 When an alkali metal dissolves in liquid ammonia the solution acquires different colours. Explain the reasons for this type of colour change.

12.9 What is meant by 'diagonal relationship' in the periodic table? What is it due to?

12.10 Describe in detail the manufacture of sodium carbonate by the Solvay process. State the principles involved in this process.

12.11 Describe three industrial uses of caustic soda. Describe one method of manufacture of sodium hydroxide. What happens when sodium hydroxide reacts with (i) aluminium metal (ii) CO_2 (iii) SiO_2.

12.12 Why is it that the *s*-block elements never occur free in nature? What are their usual modes of occurrence and how are they generally prepared?

12.13 Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals
(a) nitrates
(b) carbonates
(c) sulphates.

12.14 Explain what happens when
(i) sodium hydrogen carbonate is heated
(ii) sodium amalgam reacts with water
(iii) fused sodium metal reacts with ammonia.

12.15 Mention the general trends in Group 1 and in Group 2 with increasing atomic number with respect to
(a) density
(b) melting point
(c) atomic size
(d) ionization enthalpy.

12.16 Starting with sodium chloride how would you proceed to prepare (state the steps only)
(i) sodium metal
(ii) sodium hydroxide
(iii) sodium peroxide
(iv) sodium carbonate.

12.17 State as to why
(i) lithium on being heated in air mainly forms the monoxide and not the peroxide
(ii) an aqueous solution of sodium carbonate gives alkaline tests
(iii) sodium is prepared by electrolytic method and not by chemical method.

12.18 How do the following properties change on moving form Group 1 to Group 2 in the periodic table?
(i) Atomic size
(ii) Ionization enthalpy
(iii) Density
(iv) Melting points.

12.19 Like lithium in Group1, beryllium shows anomalous behaviour in Group 2. Write three such properties of beryllium which make it anomalous in the group.

12.20 Beryllium exhibits some similarities with aluminium. Point out three such properties.

12.21 'The chemistry of beryllium is not essentially ionic'. Justify the statement by making a reference to the nature of oxide, chloride and fluoride of beryllium.

12.22 Name the chief forms of occurrence of magnesium in nature. How is magnesium extracted from one of its ores?

12.23 Commercial aluminium always contains some magnesium. Name two such alloys of aluminium. What properties are imparted by the addition of magnesium to these alloys?

12.24 Comment on each of the following observations:
(a) The mobilities of the alkali metal ions in aqueous solution are $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$
(b) Lithium is the only alkali metal to form a nitride directly
(c) E^0 for $M^{2+}(aq) + 2e \longrightarrow M(s)$ (where M= Ca, Sr or Ba) is nearly constant.
(d) LiF is least soluble among the fluorides of alkali metals.

12.25 Why does the following reaction

$$\text{C - Cl} + \text{MF} \longrightarrow \text{C - F} + \text{MCl}$$

proceed better with KF than with NaF?

12.26 The enthalpy of formation of hypothetical CaCl(s) theoretically found to be -188 kJ mol^{-1} and the $\Delta_f H^\ominus$ for $CaCl_2(s)$ is -795 kJ mol^{-1}. Calculate the $\Delta_f H^\ominus$ for the disproportionation reaction.

$$2CaCl\ (s) \longrightarrow CaCl_2(s) + Ca(s)$$

[Hint: ($\Delta_f H^\ominus$ ($CaCl_2$) -2 $\Delta_f H^\ominus$ (CaCl)] (Answer : -419kJ mol^{-1})

12.27 Compare and contrast the chemistry of Group 1 metals with that of Group 2 metals with respect to
(i) nature of oxides
(ii) solubility and thermal stability of carbonates
(iii) polarizing power of cations
(iv) reactivity and reducing power.

12.28 Describe the importance of the following:
(i) limestone(ii) cement (iii) plaster of paris

12.29 Mention the main constitutes of Portland cement.

12.30 What happens when
(i) magnesium is burnt in air
(ii) quicklime is heated with silica
(iii) chlorine reacts with slaked lime
(iv) calcium nitrate is heated.

12.31 Describe two important uses of each of the following
(i) caustic soda
(ii) sodium carbonate
(iii) quicklime.

12.32 Draw the structure of
(i) $BeCl_2$ (vapour) (ii) $BeCl_2(s)$.

12.33 List the raw material's required in the manufacture of Portland cement. What is the role of gypsum in it ?

12.34 State as to why
(a) A solution of Na_2CO_3 is alkaline
(b) Alkali metals are prepared by electrolysis of their fused chlorides.
(c) Sodium is found more useful than potassium.

12.35 Write balanced equations for reactions between
(a) Na_2O_2 and water
(b) KO_2 and water
(c) Na_2O and CO_2

12.36 Name an element which is invariably bivalent and whose oxide is soluble in excess of NaOH and its dipositive ion has a noble gas core.

12.37 Differentiate between (a) quick-lime (b) lime-water (c) slaked-lime.

12.38 How is Plaster of Paris prepared? Describe its chief property due to which it is widely used.

12.39 How would you explain?
(i) BeO is insoluble but $BeSO_4$ in soluble in water
(ii) BaO is soluble but $BaSO_4$ is insoluble in water
(iii) LiI is more soluble than KI in ethanol
(iv) $NaHCO_3$ is known in solid state but $Ca(HCO_3)_2$ is not isolated in solid state.

12.40 Contrast the action of heat on the following and explain your answer :
(i) Na_2CO_3 and $CaCO_3$
(ii) $MgCl_2.6\ H_2O$ and $CaCl_2.6H_2O$
(iii) $Ca(NO_3)_2$ and $NaNO_3$

12.41 Complete the following equations for the reaction between
(i) $Ca + H_2O$
(ii) $Ca(OH)_2 + Cl_2$
(iii) $BeO + NaOH$
(iv) $BaO_2 + H_2SO_4$

UNIT 13

SOME p-BLOCK ELEMENTS : BORON, CARBON, NITROGEN AND OXYGEN

Objectives

After studying this unit, you will be able to

- understand the chemistry of boron and its compounds.
- know the allotropes of elemental carbon and the chemistry of inorganic compounds of carbon.
- understand the chemistry of nitrogen and its compounds, the manufacture, properties and uses of ammonia and nitric acid.
- understand the chemistry of oxygen and oxides.
- know the preparation, structure and oxidizing properties of ozone.

"The first element of each non-metal group differs in many respects from the other members of the group."

We learnt in Unit 4 that the elements can be classified into *s*-, *p*-, *d*- and *f*- blocks in Periodic Table on the basis of their electronic configurations. Of these, the p-block is the only one which contains non-metallic elements. The p-block elements display a wide-ranging and diverse chemistry depending on the group to which they belong. In general non-metals have higher ionization enthalpies and higher electronegativities than the metals. Hence, in contrast to metals, which readily form cations, non-metals readily form anions. The compounds formed by non-metals with metals are generally ionic in view of large differences in their electronegativities. On the other hand, compounds formed between non-metals themselves are largely covalent in character because of small differences in their electronegativities. Thus compounds resulting from the union of non-metals generally tend to be molecular in nature.

The first member of each of the groups 13-17 of the *p*-block elements differs in many respects from the other members of their respective groups. These differences are quite significant in groups 13-16. However, in group 17, the halogens show much more similarity among themselves in their chemical behaviour than the elements of other groups. What are the reasons for the different chemical behaviour of the first member of a group of elements in the *p*-block compared to that of the subsequent members in the same group? Besides its small size and high electronegativity, the first member of each group has only four valence orbitals(2*s* and 2*p*) available for bonding and seldom forms compounds in which the coordination number exceeds four. In other words, there is no expansion of the valence shell to accommodate more than four pairs of electrons. Furthermore, the first member of a group displays a greater

ability to form p_π-p_π multiple bonds to itself (e.g. C=C, C≡C, N≡N) and to other second row elements (e.g. C=O, C=N, C≡N, N=O) compared to the subsequent members of the same group. This type of π-bonding is not particularly strong for the elements of the third and subsequent rows of the Periodic Table.

In this Unit, we will study the chemistry of boron, carbon, nitrogen and oxygen, the first members of groups 13-16. Among these, carbon is central to life on our planet. Molecules of life essentially contain carbon, nitrogen and oxygen.

13.1 BORON

Boron is the first member of group 13 of the Periodic Table and is the only non-metal of this group. Its ground-state electronic configuration is $1s^2\ 2s^2\ 2p^1$ which in the excited state (B^*) is : $1s^2, 2s^1, 2p^2$. Thus boron has three electrons in its valence orbitals. Because of its small size, high ionization enthalpy and low electronegativity, boron forms a variety of covalent molecular compounds. In this respect, boron resembles carbon and silicon and differs from the other members of Group 13. However, since the number of valence electrons (three) in boron is one less than the number of valence orbitals (one *s* and three *p*), it forms compounds, especially the hydrides, which are ELECTRON DEFICIENT. Many of the boron compounds thus behave as Lewis acids, eg. BF_3 combines with the Lewis base NH_3 to give $H_3N : \rightarrow BF_3$.

13.1.1 Occurrence

Boron occurs in two isotopic forms, ^{10}B (19%) and ^{11}B (81%). The abundance of boron in the earth's crust is less than 0.001% by mass. Boron occurs mainly as borates and orthoboric acid. The important minerals of boron are BORAX, $Na_2[B_4O_5(OH)_4].8H_2O$, KERNITE, $Na_2[B_4O_5(OH)_4]$ and COLEMANITE $[CaB_3O_4(OH)_3].H_2O$. Commercially viable deposits of borates are found in California (U.S.A.) and Turkey. In India, borax occurs in Puga Valley, Ladakh and Sambhar Lake, Rajasthan.

13.1.2 Isolation

Four important methods for the preparation of elemental boron are :

(a) reduction of boron oxide by an electropositive metal.

$$B_2O_3(s) + 3Mg(s) \longrightarrow 2B(s) + 3MgO(s)$$

(b) electrolytic reduction of fused borates or tetrafluoroborates (KBF_4) in molten KCl/KF at 1073 K.

(c) the reduction of a volatile boron compound by dihydrogen at high temperature on a heated tantalum filament.

$$2BCl_3(g) + 3H_2(g) \xrightarrow{1270K} 2B(s) + 6HCl(g)$$

Boron of high purity (~ 99.9%) can be prepared by this method.

(d) By thermal decomposition of boranes and boron halides at temperatures ~ 1173 K.

Example 13.1

Write balanced equation for the preparation of elemental boron by reduction of BBr_3 with dihydrogen.

Solution

$$2BBr_3(g) + 3H_2(g) \rightarrow 2B(s) + 6H\ Br(g)$$

13.1.3 Physical Properties

Boron is an extremely hard, low density solid with a melting point greater than 2450 K and low electrical conductivity. Elemental boron exists in several different modifications. The phenomenon of existence of different forms of an element is called ALLOTROPY. At least four allotropes of boron may be obtained under different conditions. However the transition between different forms is an extremely slow process. All boron allotropes have structures built up of B_{12} icosahedral units shown in Fig.13.1.

13.1.4 Chemical Properties and Reactions

The chemical reactivity of boron depends markedly on the state of its subdivision and temperature. Boron reacts with fluorine at room temperature and is superficially attacked by oxygen, otherwise it is inert. At higher temperature, boron reacts with almost all non-metals except hydrogen and noble gases. It also reacts directly with almost all metals at elevated temperatures, the few exceptions being the heavier metals like Ag, Au, Cd, Hg, Sn, Pb, Sb and Bi.

Boron resists the action of fused NaOH up to 773 K, though it is dissolved by fused

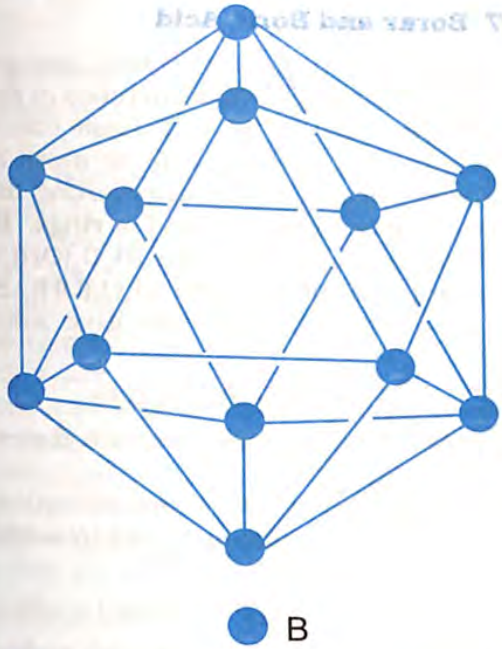


Fig.13.1 *The B_{12} icosahedral unit, the basic building block of the structures of allotropes of boron. The icosahedron is a regular polyhedron having 20 faces.*

$Na_2CO_3/NaNO_3$ mixture at 1173 K. A mixture of concentrated H_2SO_4 and HNO_3(2 : 1) is also effective in dissolving elemental boron. However, boron does not react with non-oxidizing acids.

13.1.5 Boron Hydrides

In view of the trivalency of boron, we would expect it to form a simple hydride, BH_3, which however does not exist. The simplest boron hydride known is diborane, B_2H_6. Besides diborane, boron forms a number of higher hydrides known as BORANES; most of them have molecular formulae corresponding to B_nH_{n+4} and B_nH_{n+6}. The chemistry of diborane is considered in some detail here.

Diborane, B_2H_6

One method of preparing diborane is to treat boron trifluoride with $LiAlH_4$ in diethyl ether:

$$4BF_3 + 3\,LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

A convenient laboratory method for the preparation of diborane involves the oxidation of sodium borohydride with iodine:

$$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$$

Diborane is produced on an industrial scale by the reaction of BF_3 with sodium hydride

$$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$$

The higher boranes are formed when B_2H_6 is heated at 373-523 K.

Diborane is a colourless, highly toxic gas with a b.p. of 180K. Diborane catches fire spontaneously upon exposure to air. It burns in oxygen releasing an enormous amount of energy

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O;\ \Delta_cH^\ominus = -1976\ kJmol^{-1}$$

Most of the higher boranes are also spontaneously flammable in air. Boranes are readily hydrolyzed by water to give boric acid.

$$B_2H_6(g) + 6H_2O(l) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$$

Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts $BH_3 . L$

$$B_2H_6 + 2\,NMe_3 \rightarrow 2BH_3 . NMe_3$$

$$B_2H_6 + 2\,CO \rightarrow 2BH_3 . CO$$

Reaction of ammonia with diborane gives initially $B_2H_6.2NH_3$ formulated as $[BH_2(NH_3)_2]^+[BH_4]^-$; further heating gives borazine, $B_3N_3H_6$ known as "inorganic benzene" in view of its ring structure with alternate BH and NH groups.

$$3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^-$$

$$\downarrow \text{ heat}$$

$$2B_3N_3H_6 + 12H_2$$

The structure of diborane is shown in Fig.13.2(a). The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre–two electron bonds shown in Fig.13.2 (b).

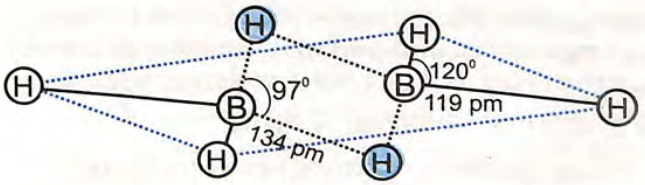


Fig.13.2(a) *The structure of diborane, B_2H_6*

Boron also forms a series of hydridoborates ; the most important one is the tetrahedral $[BH_4]^-$ ion.

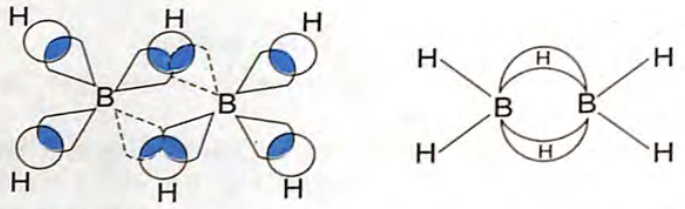


Fig.13.2(b) *Bonding in diborane. Each B atom uses sp^3 hybrids for bonding. Out of the four sp^3 hybrids on each B atom, one is without an electron shown in broken lines. The terminal B-H bonds are normal 2c-2e bonds but the two bridge bonds are 3c-2e bonds. The 3c-2e bridge bonds are also referred to as banana bonds.*

Tetrahydridoborates of several metals are known. Lithium and sodium tetrahydridoborates, also known as ***borohydrides***, are prepared by the reaction of metal hydrides with B_2H_6 in diethyl ether.

$$2MH + B_2H_6 \rightarrow 2\,M^+[BH_4]^-$$
$$M = Li \text{ or } Na$$

Both $LiBH_4$ and $NaBH_4$ are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

13.1.6 Boron halides

The boron trihalides have the general formula BX_3 which are monomeric covalent species. They are planar and bonding can be explained in terms of sp^2 hybridization. They do not dimerize like BH_3 because the lone pairs on the halogens can interact with the vacant p orbital on boron.

Boron trifluoride is obtained by heating B_2O_3 with CaF_2 and concentrated sulphuric acid :

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \rightarrow 2BF_3 + 3CaSO_4 + 3H_2O$$

The other boron halides are prepared by direct union of the elements at elevated temperatures.

The boron halides fume in moist air and are highly sensitive to moisture. Boron trifluoride undergoes slow and partial hydrolysis with water but the other halides react violently with water

$$BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl$$

Boron halides are strong Lewis acids and form adducts with bases such as amines, ethers, sulphides or phosphines.

$$BX_3 + NR_3 \rightarrow X_3B.NR_3$$

Because of its strong Lewis acid character, BF_3 is used as a catalyst in several industrial processes.

13.1.7 Borax and Boric Acid

Boron forms strong bonds with oxygen as reflected in the invariable occurrence of *borates* in nature (section 13.1.1). The basic structural unit in borates can have one or more boron atoms linked together by intervening oxygen atoms in the form of chains and or rings. ***Borax*** contains the tetranuclear units $[B_4O_5(OH)_4]^{2-}$; its correct formula is therefore $Na_2[B_4O_5(OH)_4].8H_2O$. Borax dissolves in water to give alkaline solutions:

$$Na_2B_4O_7 + 2H_2O \rightarrow 2NaOH + H_2B_4O_7$$

Borax is therefore used as a water softener and cleansing agent.

Boric acid is the trivial name for orthoboric acid, H_3BO_3. It is usually prepared by acidifying an aqueous solution of borax :

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$$

Boric acid is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.). It is a white crystalline substance. It has a layer structure in which planar BO_3 units are joined by hydrogen bonds as shown in Fig.13.3.

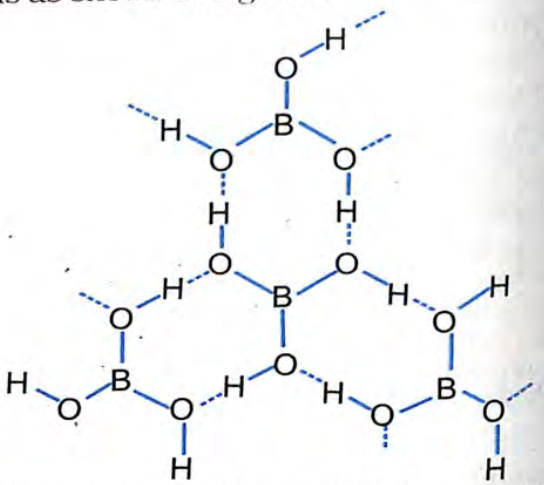


Fig.13.3 *Structure of boric acid; the dotted lines represent hydrogen bonds*

Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion :

$$B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H_3O^+$$

Heating orthoboric acid above 370 K leads to partial removal of water to yield metaboric acid, HBO_2; further heating yields boric oxide, B_2O_3 which is the principal oxide of boron.

$$H_3BO_3 \overset{373K}{\rightleftharpoons} HBO_2 \overset{>373K}{\rightleftharpoons} B_2O_3$$

13.1.8 Uses of Boron and its Compounds

The main industrial application of borax and boric acid is in the manufacture of heat-resistant borosilicate glass (e.g. Pyrex). Borax is also used as a flux for soldering metals and for making porcelain enamels. A solution of boric acid in water is commonly used as a mild antiseptic. Because of the very high ability of boron-10 (^{10}B) isotope to absorb neutrons, metal borides are used in nuclear industry as protective shields and control rods. This special property of ^{10}B isotope to absorb neutrons is also of current interest in the possible use of boron compounds in cancer chemotherapy. Boron fibres are used in making light, composite materials for aircraft.

13.2 CARBON

Carbon, the first member of group 14 has the ground state electronic configuration, [He] $2s^2 2p^2$. Carbon is a typical non-metal forming covalent bonds in the vast majority of its compounds by making use of all its four valence electrons. A remarkable feature of carbon is its ability to form compounds in which carbon atoms are linked to each other in chains or rings. This property is called **catenation**. Carbon also forms p_π- p_π multiple bonds to itself and to other elements, particularly nitrogen and oxygen. Thus carbon forms an extensive range and variety of compounds, both naturally-occurring and man-made, and these run into several millions. Carbon compounds are treated as a separate branch of chemistry called **ORGANIC CHEMISTRY** (Units 14-17). However, the compounds in which carbon is combined with metals and metalloids, simple binary compounds with non-metals and those, which do not contain carbon-hydrogen bonds are traditionally regarded as inorganic compounds. Some examples of such compounds are calcium carbide, silicon carbide, carbon monoxide, carbon dioxide, hydrogen cyanide, and salts containing carbonate, bicarbonate and cyanide ions. The chemistry of the element itself in its various allotropic forms is also considered to be in the realm of inorganic chemistry. In this section, we will first deal with the various allotropic forms of carbon and then briefly outline the chemistry of a few inorganic compounds of carbon.

13.2.1 Occurrence of Carbon

Carbon ranks seventeenth in the order of abundance in the earth's crust. It is widely distributed in nature in the form of coal, petroleum and metal carbonates of electropositive metals. All living systems contain carbon compounds. Carbon is also present as CO_2 in the atmosphere.

Naturally occurring carbon contains two stable isotopes ^{12}C (98.9%) and ^{13}C (1.1 %) in addition to traces of the radioactive ^{14}C isotope. The isotope ^{14}C has a half-life of 5770 years and is used in **radiocarbon dating** to determine the age of archaeological specimens of organic origin. The isotope ^{12}C is the international standard for atomic mass measurement and assigned a mass of 12.00000 units.

13.2.2 Allotropes of Carbon

Elemental carbon provides a very good example of the phenomenon of **ALLOTROPY**. It exists in several crystalline and amorphous forms. Until 1985 the two well-known allotropes of carbon were **diamond** and **graphite**. In that year, a third form of carbon known as **fullerenes** were discovered by H.W. Kroto, R.F. Curl and R.E. Smalley. This exciting discovery has heralded a new era in chemistry. The fullerenes consist of hollow cages of carbon atoms. They are large spheroidal molecules of composition C_{2n} ; two important members of this family are C_{60} and C_{70}. The 1996 Nobel Prize in chemistry was awarded to the above scientists for the discovery of fullerenes –the new form of carbon .

Diamond is a very hard crystalline solid. In its crystalline lattice, each carbon atom is linked to four other carbon atoms tetrahedrally by using sp^3 hybrid orbitals giving rise to a rigid three dimensional network of carbon atoms (see Fig.13.4). Since covalent bonds are strong and directional and they extend throughout the crystal, it is very difficult to deform or break the crystal lattice. Hence diamond is an extremely hard substance.

Graphite has a layer structure (see Fig.13.5) in which each carbon is bonded to three other carbon atoms to form a hexagonal sheet. Each carbon atom forms three sigma bonds by means of sp^2 hybrid orbitals. The remaining unhybridised p-orbital of each carbon atom having an electron overlaps with its counterparts

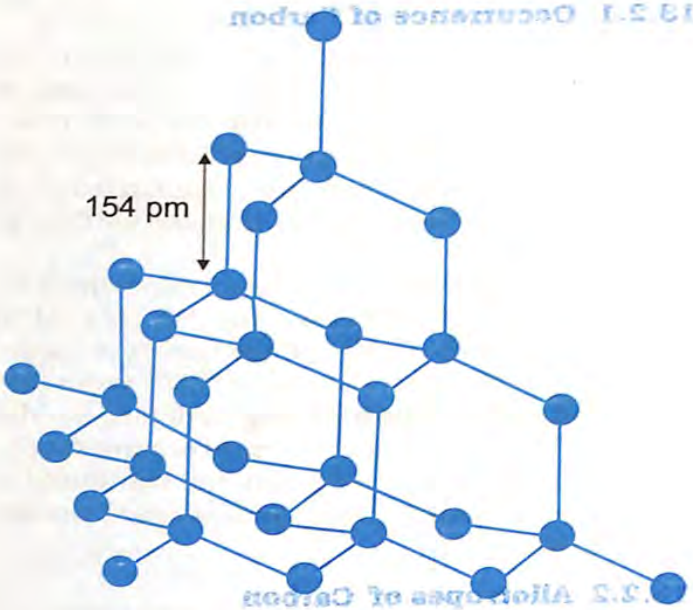


Fig.13.4 The structure of diamond

on the adjacent carbon atoms in the same layer to form π-bonds. The C-C bond distance within the hexagonal layer is 142 pm which corresponds to a C-C bond order of 1.33. The hexagonal sheets are held together by weak van der Waals forces. Since it is easy for one layer to slide over another, graphite is a soft and slippery material with excellent lubricating properties. The π-electrons within the layer are free to move and this accounts for the electrical conductivity of graphite. The different structures adopted by diamond and graphite thus nicely explain their contrasting properties. Whereas diamond is hard, transparent and a non-conductor of electricity, graphite is soft, opaque, and a good conductor of electricity.

Fullerenes were originally made by the evaporation of graphite using a laser. A more practical method involves the heating of graphite in an electric arc in the presence of an inert gas such as helium or argon. The sooty material formed by condensation of vapourised C_n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of other fullerenes consisting of even number of carbon atoms upto 350 or above. C_{60} and C_{70} can be readily separated from the fullerene soot by extraction in toluene followed by chromatographic separation over alumina. In contrast to graphite or diamond, the fullerenes dissolve in organic solvents to give

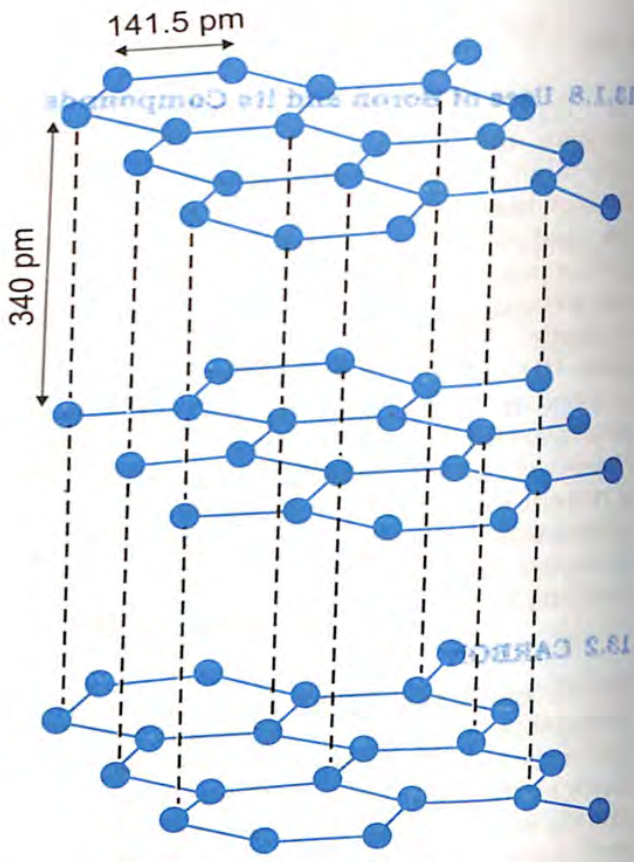


Fig.13.5 The structure of graphite

coloured solutions. A solution of C_{60} in toluene is purple whereas that of C_{70} is orange-red. In fact, fullerenes are the only pure form of carbon because they do not have "dangling" edge or surface bonds to be attracted to other atoms as is the case with diamond or graphite.

The beautiful structure of C_{60} is shown in Fig. 13.6. It has been named BUCKMINSTER-FULLERENE in honour of American architect, Robert Buckminster Fuller who designed geodesic dome structures having hexagonal and pentagonal patterns. The general name FULLERENE refers to the family of spheroidal carbon cage molecules. The shape of C_{60} resembles that of a soccer ball. It contains twelve five-membered rings and twenty six-membered rings. Six-membered rings are fused both to other six membered rings and five membered rings, but the five-membered rings are connected only to six-membered rings. All the carbon atoms are equivalent. There are both single and double bonds with C-C distances of 145.3 and 138.3 pm respectively.

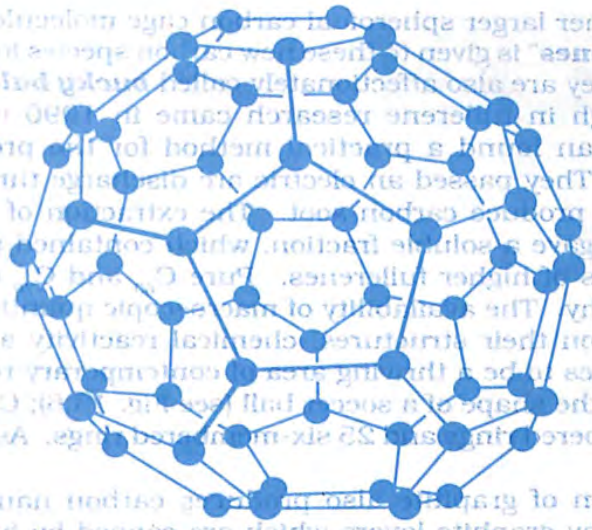


Fig.13.6 The structure of C_{60}, Buckminsterfullerene : Note that the molecule has the shape of a soccer ball (football)

BUCKY BALLS AND BUCKY TUBES : THE FULLERENE SAGA

The 1996 Nobel Prize in Chemistry was shared by two American Scientists, Richard E. Smalley and Robert F. Curl of Rice University, Huston, Texas, U.S.A. and a British scientist, Harold W. Kroto of the University of Sussex, Brighton, England for their discovery of fullerenes in 1985. This discovery provides a fascinating chronicle in modern chemistry and is a shining example of collaborative research by scientists hailing from different scientific disciplines leading to spectacular results. No other discovery in recent years has excited the interest and imagination of chemists, physicists and material scientists as much as that of fullerenes.

It is an interesting story how the three scientists came together to carry out their research that led to the discovery of fullerenes. Kroto for long worked on microwave spectroscopy and had shown that linear chain molecules of carbon and nitrogen [cyano polyynes HC_nN (n = 5-11)] were present in interstellar space. He was on the look out for a method to produce long carbon chains in the laboratory to probe how such chain molecules are formed in space. Smalley was an authority on cluster chemistry and had built up an apparatus to produce clusters of virtually any element in the periodic table by "laser vaporization supersonic beam" technique. Curl was an expert in laser spectroscopy of molecules and transient species and he and Smalley were collaborating from 1982 on semiconductor clusters. Kroto mentioned his idea to his friend Curl who told him that Smalley's apparatus was ideally suited to produce the carbon clusters which Kroto was searching for. Kroto had the idea, Smalley had the apparatus and Curl brought the two together. The crucial experiments that culminated in the discovery of fullerenes were carried out in Rice University during September 1 – September 12, 1985 with the assistance of the graduate students James R. Heath and Sean C. O'Brien.

Laser evaporation of graphite did produce evidence for the formation of linear molecules with 5-9 carbon atoms, which had been observed in interstellar space. In addition, several other carbon clusters containing forty to hundred (always an even number) of carbon atoms were formed. The researchers were using mass spectrometry as an analytical tool to identify the composition of the species formed. They noticed that one peak at atomic mass unit (u) 720 corresponding to C_{60} was predominantly present in the evaporation experiments. Another less prominent peak was observed at 840 u. corresponding to C_{70}. The researchers made the daring proposal that the peak at 720 u. arose from a new cage form of carbon (C_{60}). They christened the molecule **"Buckminsterfullerene"** in honour of the American architect Buckminster Fuller, who designed geodesic domes. Subsequent research in various countries

led to the discovery of other larger spheroidal carbon cage molecules and carbon nanotubes. The general name "**fullerenes**" is given to these new carbon species formed by the condensation of the carbon vapour. They are also affectionately called ***bucky balls*** and ***bucky tubes***.

The next breakthrough in fullerene research came in 1990 when the astrophysicists Kraetechmer and Huffman found a practical method for the production of fullerenes in macroscopic quantities. They passed an electric arc discharge through graphite rods in an atmosphere of helium to produce carbon soot. The extraction of the soot with an organic solvent such as benzene gave a soluble fraction, which contained mainly C_{60} with a smaller quantity of C_{70} and traces of higher fullerenes. Pure C_{60} and C_{70} can be isolated from this fraction by chromatography. The availability of macroscopic quantities of C_{60} and C_{70} led to a large number of studies on their structures, chemical reactivity and possible applications. Fullerene science continues to be a thriving area of contemporary research.

The molecule of C_{60} has the shape of a soccer ball (see Fig. 13.6); C_{70} resembles a rugby ball. It consists of 12 five-membered rings and 25 six-membered rings. As in C_{60}, the pentagons are isolated from each other.

Electric arc evaporation of graphite also produces carbon nanotubes which consist of cylindrical tubes formed by graphite layers which are capped by fullerene-like hemispheres. This has triggered worldwide interest in studying the physical properties of carbon nanotubes and their potential applications in catalysis, nanotechnology and electronics.

In the words of Kroto, "the marriage of ideas resulting from the discoveries of carbon chains in space with the recognition that the cluster beam technique might offer laboratory support for their circumsteller origin led to "the serendipitous discovery in 1985 that the C_{60} molecule not only existed but that it self-assembled". Rightly, Kroto calls C_{60} "the celestial sphere that fell to earth".

Fig.A Richard E. Smalley

Fig.B Robert F. Curl

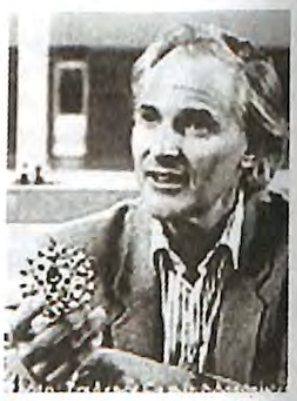


Fig.C Harold W. Kroto

Graphite is thermodynamically the most stable allotrope of carbon. Its standard enthalpy of formation ($\Delta_f H^\ominus$) is assigned a value of zero. The standard enthalpy of formation ($\Delta_f H^\ominus$)of diamond and C_{60} are 1.90 and 38.1 kJ mol^{-1}, respectively.

Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes. Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

13.2.3 Uses of Carbon

The uses of various allotropic forms of carbon are given in Table 13.1. As yet, no practical uses have been found for fullerenes although several nanotechnological applications are projected.

13.2.4 Inorganic Carbon Compounds

Oxides of Carbon

Two well-known oxides of carbon are **carbon monoxide**, CO and **carbon dioxide**, CO_2. Carbon monoxide is formed by the incomplete combustion of carbon or carbon-containing fuels. It is

Table 13.1 Uses of Various Allotropic Forms of Carbon

Forms of carbon	Uses
Diamond	Gemstone, cutting, drilling, grinding, polishing, industry
Graphite	Steel manufacture (reducing agent) refractories, pencils, high temperature crucibles, electrodes in electrolytic extraction of elements, moderator in nuclear reactors, high-strength composite materials.
Coke	Steel manufacture, fuel
Carbon black	Rubber industry, pigments in ink, paints and plastics
Activated carbon	Decolorizing agent in sugar industry, purification of chemicals and gases by absorption, catalyst.
Charcoal	Fuel, reducing agent

invariably present in automobile exhaust gases.

$$C(s) + \tfrac{1}{2} O_2(g) \rightarrow CO(g)$$

The pure gas is prepared on a smaller scale by dehydrating pure formic acid with concentrated sulphuric acid

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

Carbon monoxide is commercially produced by the passage of steam over hot coke. This reaction also produces hydrogen and the mixture of CO and H_2 is known as **water gas** or **synthesis gas**.

$$C(s) + H_2O(g) \rightarrow \underset{\text{(water gas)}}{CO(g) + H_2(g)}$$

When air is used instead of steam, a mixture of CO and N_2 are produced which is called **producer gas**

$$4C(s) + \underset{\text{air}}{O_2(g) + 4N_2(g)} \rightarrow \underset{\text{(producer gas)}}{2\,CO(g) + 4N_2(g)}$$

Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat. Water gas and producer gas are thus industrially important fuel gases. Water gas is also very important commercially for the manufacture of methanol and acetic acid.

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)\ \Delta_r H^\ominus = -566\ kJ\ mol^{-1}$$

Carbon monoxide is a colourless, odourless and an extremely poisonous gas. It binds tightly to the iron atom of the hemoglobin in red blood cells and thereby inhibits their ability to bind with oxygen and carry it to the brain and other body tissues.

Carbon monoxide is a powerful reducing agent and reduces metal oxides to the corresponding metals.

$$Fe_2O_3 + 3\,CO \xrightarrow{1273K} 2Fe + 3CO_2$$

It readily combines with chlorine in sunlight to give carbonyl chloride (phosgene , another poisonous gas).

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

Carbon monoxide also combines with some transition metals to form gaseous carbonyls. The carbonyl formed with nickel, $Ni(CO)_4$, is of industrial importance.

Carbon dioxide is formed in the combustion of carbon and other fossil fuels in an excess of oxygen

$$C\,(s) + O_2(g) \rightarrow CO_2(g)$$

$$C_5H_{12}(g) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(g)$$

Commercially CO_2 is produced as a by-product of ammonia manufacture for which hydrogen is produced by the reactions shown below:

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

$$CH_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4H_2(g)$$

In the laboratory, CO_2 is produced by the action of acids on carbonates:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

Carbon dioxide is also formed during fermentation.

Carbon dioxide is a colourless gas. It is heavier than air with a density of 1.977 g/L at 273 K. Unlike carbon monoxide, CO_2 is not poisonous but does not support life in humans or animals. It can cause suffocation and eventually death on account of lack of oxygen. Carbon dioxide is slightly soluble in water. The solubility increases with pressure. Soda water and other aerated soft drinks are solutions of CO_2 in water under pressure.

Carbon dioxide is a weakly acidic oxide. When it dissolves in water, only some of the molecules react with water to form carbonic acid, H_2CO_3, and a greater part of dissolved CO_2 remains loosely hydrated. Carbonic acid is a weak dibasic acid. It forms two series of salts, the hydrogen carbonates and carbonates derived from the anions HCO_3^- and CO_3^{2-}. Thus CO_2 is the anhydride of carbonic acid.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^- aq \rightleftharpoons H^+ + CO_3^{2-}(aq)$$

Thus a solution of carbon dioxide in water is an equilibrium mixture of CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}. These equilibria are relevant in connection with the role of carbonic acid – hydrogen carbonate ion buffer system in maintaining the pH of human blood. Furthermore the rate at which CO_2 comes into equilibrium with H_2CO_3 is slow and this is also important in the physiology of CO_2.

Example 13.2

Because carbonic acid is a weak acid, solutions of metal carbonates or hydrogen carbonates are alkaline. Write balanced equations for the hydrolysis of HCO_3^- and CO_3^{2-} ions.

Solution

$$CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^-$$

$$HCO_3^- + H_2O \rightleftharpoons OH^- + H_2CO_3$$

Carbonates of many metals are known but only the bicarbonates of the alkali metals exist in the solid state. Bicarbonates of calcium and magnesium are responsible for the temporary hardness of water (see Unit 11). Several carbonates such as $Na_2CO_3.10H_2O$ (washing soda), K_2CO_3, $CaCO_3$ and $NaHCO_3$ (baking soda) are commercially important chemicals. The manufacture and uses of some of these carbonates are discussed in Unit 12.

The structures of carbonic acid, HCO_3^- ion and CO_3^{2-} ion contain a central carbon atom in a trigonal planar geometry. The carbon atom forms three σ bonds to three oxygen atoms by using its sp^2 hybrid orbitals; the unhybridized *p*-orbital on the carbon atom is delocalised over the *p*-orbitals of the three oxygen atom to form π-bonds (see Unit 6).

The main application of CO_2 is as a refrigerant. Solid carbon dioxide can sublime to the gaseous state without passing through the liquid stage and hence is called DRY ICE. It is used as a coolant for preserving perishable food items such as meat. It is also a convenient laboratory cooling agent for carrying out reactions below 273 K. In recent years, supercritical CO_2* is used as a solvent to extract organic compounds from their natural sources (e.g. caffeine from coffee beans; perfumes from flowers) or to carry out industrially important reactions. Another major use of CO_2 is in the manufacture of urea by reaction with NH_3

$$CO_2 + 2NH_3 \rightarrow \underset{\text{Ammonium carbamate}}{NH_2CO_2NH_4} \rightarrow \underset{\text{urea}}{CO(NH_2)_2}$$

Carbon dioxide is also used in fire extinguishers.

13.2.5 Carbides

Binary compounds of carbon with more electropositive elements than itself (except hydrogen) are called carbides. Three types of carbides are known. They are:

(a) Ionic carbides : These are formed by the highly electropositive metals belonging to the alkali and alkaline earth groups and aluminium. An important carbide belonging to this group is calcium carbide CaC_2, which is prepared by the reaction of calcium oxide with carbon at high temperature. Calcium carbide reacts with water liberating acetylene gas used for welding.

* *A substance above its critical pressure is called a supercritical fluid. Although it is a gas, it is very dense and can behave as a solvent. A gaseous substance can be liquified by applying pressure only if it is below its critical temperature. For CO_2, the critical pressure and temperature are $73 \times 1.013 \times 10^5$ Pa and 304 K respectively.*

$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2$

(b) Interstitial carbides: Carbides formed by transition metals belong to this category. In these compounds, the carbon atoms occupy interstitial voids in the close packed lattice of metal atoms. Carbides of this type are extremely hard and electrically conducting. A typical example is tungsten carbide(WC). It is used to make cutting and drilling tools.

(c) Covalent carbides: These are formed by metalloids such as silicon and boron. Silicon carbide is known as carborundum and is used for making cutting tools and abrasives.

13.2.6 Carbon-nitrogen Compounds

An important compound containing both carbon and nitrogen is calcium cyanamide, $CaCN_2$. It is obtained by the reaction of calcium carbide with nitrogen at 1373 K.

$$CaC_2(s) + N_2(g) \rightarrow CaNCN(s) + C(s)$$

Calcium cyanamide is used as a fertilizer. It is also used for the manufacture of melamine plastics. Calcium cyanamide is the starting material for the manufacture of sodium cyanide obtained by fusing it with carbon and sodium carbonate

$$CaCN_2 + C + Na_2CO_3 \rightarrow CaCO_3 + 2NaCN$$

Sodium cyanide is used for the extraction of gold and silver from their ores. Treatment of sodium cyanide with strong acids liberates HCN which is a colourless gas and behaves as a weak acid in aqueous solution (pK_a=9.0). Industrially, HCN is obtained by the reaction of ammonia with methane at a high temperature:

$$CH_4(g) + NH_3(g) \xrightarrow[1500K]{\text{Pt catalyst}} HCN(g) + 3H_2(g)$$

Cyanides and HCN are extremely *poisonous* substances. Ingestion or inhalation can lead to instant death. HCN is used in the manufacture of methylmethacrylate polymers and adiponitrile, which is an intermediate for nylon.

Two other carbon-nitrogen compounds also deserve mention. These are *cyanogen*, $(CN)_2$ and *cyanamide*, H_2NCN. Cyanogen has a superficial resemblance to halogens (X_2) and is referred to as a *pseudohalogen*. Cyanogen is produced by the oxidation of HCN by O_2 using a silver catalyst or by the oxidation of CN^- by Cu^{2+}.

$$4HCN + O_2 \rightarrow 2(CN)_2 + 2H_2O$$

$$2Cu^{2+} + 4CN^- \rightarrow 2Cu(CN) + (CN)_2$$

Cyanogen is a colourless poisonous gas like HCN. It is linear and disproportionates in basic solution to cyanide and cyanate ions.

$$(CN)_2 + 2OH^- \rightarrow CN^- + OCN^- + H_2O$$

Treatment of CaNCN with water gives cyanamide (H_2NCN), which is solid, m. p. 318 K.

$$CaNCN + H_2O \rightarrow CaO + H_2NCN$$

13.3 NITROGEN

Nitrogen is the first element of group 15 of the periodic table and has the electronic configuration, $1s^2 2s^2 2p^3$. It has five valence electrons. Nevertheless, the maximum number of covalent bonds formed by nitrogen is limited to four (e.g., NH_4^+ salts). Like oxygen and hydrogen, nitrogen exists in its elemental form as a diatomic molecule (N_2). It is a typical non-metal with a high electronegativity next only to that of fluorine and oxygen. Nitrogen forms a variety of compounds in all oxidation states ranging from –3 to +5. The common oxidation states are –3 (e.g., NH_3 or Mg_3N_2), +3 (e.g., $NaNO_2$) and +5 (e.g., N_2O_5, HNO_3). The properties of atomic and molecular nitrogen are given in Table 13.2.

Table 13.2 Atomic and Molecular Properties of Nitrogen

Atomic Properties		Molecular Properties	
Ionization enthalpy/kJ mol^{-1}	1402	Melting point/K	63
Electron gain enthalpy/kJ mol^{-1}	7	Boiling point/K	77
Electronegativity	3.0	Density/g/cm^3 at 63 K	0.879
Atomic radius/pm	70	Bond length/pm	109.8
Ionic radius (N^{3-})/pm	171	Bond enthalpy/kJ mol^{-1}	946

13.3.1 Nitrogen Fixation

Nitrogen is important for life processes, as it is a constituent of plant and animal proteins and genetic material. Any process by which atmospheric nitrogen is converted into a useful nitrogen compound is referred to as nitrogen fixation. Assimilation of atmospheric nitrogen (N_2) by plants occurs through two important NITROGEN FIXATION processes:

(a) During thunder storms, nitrogen and oxygen of the air combine to form nitrogen oxides, which are eventually converted into nitric acid and nitrates in the soil.

(b) Soil bacteria in the root nodules of some plants such as beans fix atmospheric nitrogen into compounds that the plant can readily utilize. This biochemical process involves an enzyme called Nitrogenase in which the active sites contain molybdenum and iron atoms.

Industrial fixation of nitrogen

The manufacture of ammonia by the Haber process represents the principal source of industrial nitrogen fixation. Much of the ammonia manufactured, is used to make fertilizers.

13.3.2 Occurrence

Molecular nitrogen comprises 78% by volume of the atmosphere. It occurs to a small extent in the earth's crust mainly as sodium nitrate, $NaNO_3$ (called Chile saltpetre) and potassium nitrate (Indian saltpetre). Its total abundance in earth including the atmosphere is 0.01% by weight.

13.3.3 Preparation of Dinitrogen

Dinitrogen is produced commercially by the liquefaction and fractional distillation of air. Liquid nitrogen (b.p. 77 K) distills out first leaving behind liquid oxygen (b.p. 90.1 K). Dinitrogen derived from air contains small amounts of oxygen and some of the noble gases. Worldwide production of dinitrogen from this source is more than 50 million tonnes per annum.

In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$$

Small amounts of NO and HNO_3 are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing dichromate. Other possible routes for dinitrogen are the thermal decomposition of ammonium dichromate and the reaction of ammonia with CuO at elevated temperatures:

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$$

$$2NH_3 + 3CuO \rightarrow N_2 + 3Cu + 3H_2O$$

Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

$$Ba(N_3)_2 \rightarrow Ba + 3N_2$$

13.3.4 Properties and Reactions of Dinitrogen

Dinitrogen is a colourless, odourless, tasteless gas. It has two stable isotopes: ^{14}N and ^{15}N. It is non-toxic. Dinitrogen has a very low solubility in water (23.2 cm^3 per one litre of water at 273 K and 1 bar pressure). Its melting and boiling points are 63.2 K and 77.0 K respectively.

Dinitrogen is chemically unreactive at ordinary temperatures. It is neither combustible nor a supporter of combustion. The N-N bond in the N_2 molecule has a formal triple bond character (Unit 6) with a bond distance of 109.8 pm and is very stable (bond dissociation energy is 946 kJ mol^{-1}).

At high temperatures, dinitrogen directly combines with some metals and non-metals to form ionic and covalent nitrides. A few typical reactions are :

$$6Li + N_2 \rightarrow 2Li_3N$$

$$3Mg + N_2 \rightarrow Mg_3N_2$$

It combines with hydrogen at about 773 K in the presence of a catalyst (Haber process) to form ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta_r H^\ominus = -92.2 \text{ kJmol}^{-1}$$

Nitrogen combines with oxygen only at very high temperature (at about 3300 K) to form nitric oxide, NO:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) ; \quad \Delta_r H^\ominus = +180 \text{ kJmol}^{-1}$$

13.3.5 Uses of Dinitrogen

The main use of dinitrogen is in the manufacture of ammonia and other industrial nitrogen chemicals (e.g. calcium cyanamide). It also finds use where the presence of an inert atmosphere is required (iron and steel industry, inert diluent

for reactive chemicals). Liquid nitrogen is used as a refrigerant to preserve biological materials, in freezing food articles and in cryosurgery.

13.3.6 Compounds of Nitrogen

Ammonia

Ammonia is manufactured by the Haber process represented by the equilibrium :

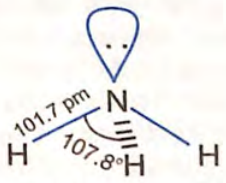
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \Delta_r H^\ominus = -92.2 \text{ kJ mol}^{-1}$$

In accordance with Le Chatelier's principle (see Unit 7), high pressure would favour the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), a temperature of around 700 K and the use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium. The flow chart for the production of ammonia is shown in Fig.13.7. Annual world production of ammonia now exceeds 100 million tonnes. In India we have several large ammonia manufacturing units.

A convenient laboratory preparation of ammonia consists of heating an ammonium salt with a strong alkali (e.g., NaOH) either in the solid form or dissolved in water. It can also be prepared by the hydrolysis of magnesium nitride.

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

Ammonia is a colourless gas with a pungent odour. Its freezing and boiling points are 198.4 K, and 239.7 K respectively. In the solid and liquid states, it is associated through hydrogen bonds as in the case of water and that accounts for its high melting and boiling points. The ammonia molecule is trigonal pyramidal with the nitrogen atom at the apex. It has three bond pairs and one lone pair as shown below.



Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the equilibrium :

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

It forms ammonium salts with acids, e.g. NH_4Cl, $(NH_4)_2SO_4$, etc. As a weak base, it precipitates the hydroxides of many metals from their solutions e.g. $Fe^{3+}(aq) + 3NH_4OH\ (aq) \rightarrow Fe(OH)_3 + 3NH_4^+(aq)$

The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It forms coordinate linkage with metal ions and the formation of such complex compounds find applications in qualitative analysis as in the case of Cu^{2+} ions :

$$\underset{\text{(blue)}}{Cu^{2+}(aq)} + 4\ NH_3(aq) \rightleftharpoons \underset{\text{(deep blue)}}{[Cu(NH_3)_4]^{2+}(aq)}$$

Ammonia is used mostly to produce various nitrogenous fertilizers (ammonium nitrate, urea,

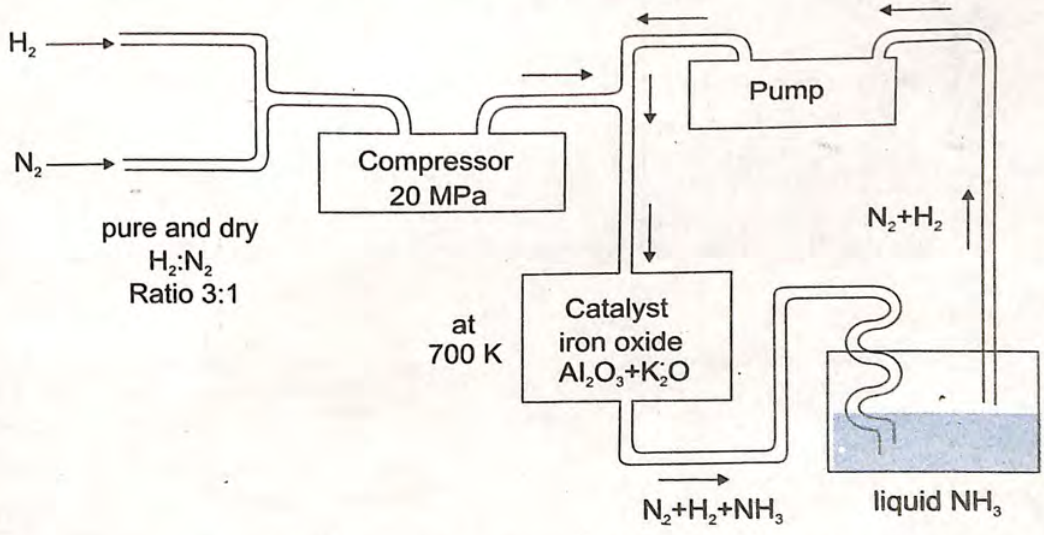


Fig.13.7 Flow chart for the manufacture of ammonia.

ammonium phosphate and ammonium sulphate) and in the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid. Liquid ammonia is also used as a refrigerant. India produces more than 1.0 million metric tonnes (in terms of nitrogen) of nitrogenous fertilizers annually. The public sector has been playing a dominant role in the fertilizer industry. At present, there are nine public sector undertakings under the Department of Fertilizers, Government of India. Many of them produce nitrogenous fertilizers (ammonium sulphate, urea, etc.).

Oxides of Nitrogen

Oxides of nitrogen provide a fascinating picture from the point of view of their varied structures and diverse chemical behaviour. They range from N_2O (oxidation state of nitrogen +1) through NO, N_2O_3, NO_2, N_2O_4 to N_2O_5 (oxidation state of nitrogen +5). The preparative routes for nitrogen oxides and their properties are given in Table 13.3.

The ability of nitrogen to form p_π-p_π multiple bonds dictates the structures of its oxides. They are also good example for illustrating the concept of RESONANCE (Unit 6). The molecular and electronic structures of oxides of nitrogen are shown in Fig. 13.8. Nitrogen monoxide is an odd-electron molecule. Because of the presence of an unpaired electron, it undergoes partial dimerization in the liquid state and exists as dimer in the solid state. Nitric oxide readily reacts with oxygen (itself a free-radical with two unpaired electrons) to give brown fumes of nitrogen dioxide (NO_2).

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Nitrogen dioxide is also an odd-electron molecule and in the gas phase, exists in equilibrium with the dimer, N_2O_4 which is colourless.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Brown — Colourless
Paramagnetic — diamagnetic

Nitrogen oxides react with water to give oxoacids of nitrogen. Thus N_2O_3 and N_2O_5 may be regarded as anhydrides of nitrous (HNO_2) and nitric acid (HNO_3) respectively. Nitrogen dioxide reacts with water to give both nitrous and nitric acids.

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

Because of its rather unreactive nature, dinitrogen monoxide (N_2O) is used as an anaesthetic, particularly in dentistry. Nitric oxide and nitrogen dioxide are important in the manufacture of nitric acid and nitrate fertilizers.

Table 13.3 Preparation and Properties of Oxides of Nitrogen

Formula	Name	Preparation	Properties
N_2O	Dinitrogen monoxide	$NH_4NO_3 \rightarrow N_2O + 2H_2O$	Colourless gas, rather unreactive
NO	Nitrogen monoxide (Nitric oxide)	$3Cu+8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$	Colourless gas, reactive, paramagnetic
NO_2	Nitrogen dioxide	$Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$	Brown gas, reactive, paramagnetic
N_2O_3	Dinitrogen trioxide	$NO + NO_2 \rightarrow N_2O_3$	Dark blue in the liquid or solid state, unstable in the gas phase
N_2O_4	Dinitrogen tetroxide	$2NO_2 \rightleftharpoons N_2O_4$	Colourless, exists in equilibrium with NO_2 both in the gaseous and liquid state
N_2O_5	Dinitrogen pentoxide	$2HNO_3 + P_2O_5 \rightarrow 2HPO_3 + N_2O_5$	Unstable as gas; in the solid state exists as $[NO_2]^+ [NO_3]^-$

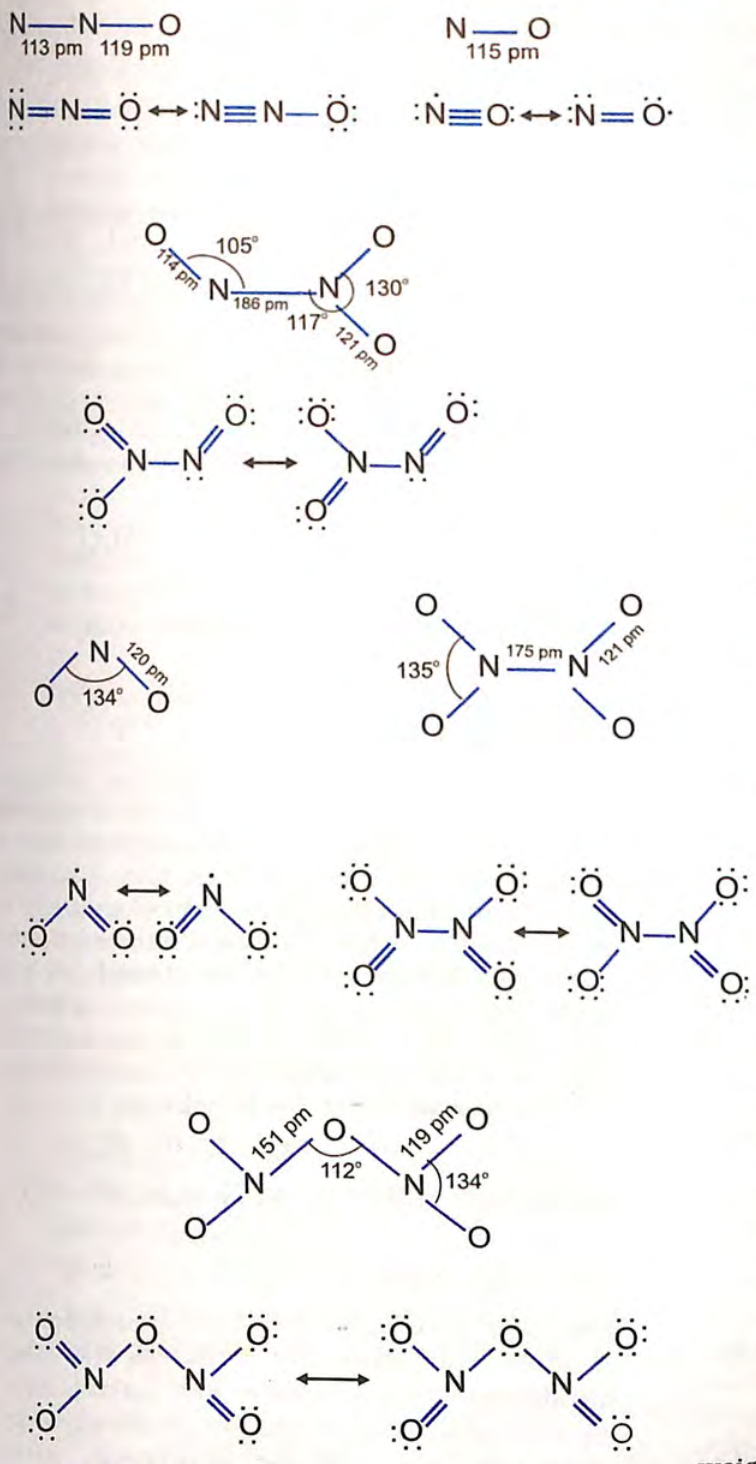


Fig.13.8 *The molecular and Lewis dot resonance structures of oxides of nitrogen.*

Liquid N_2O_4 finds use as an oxidizer for rocket fuels in missiles and space vehicles. Oxides of nitrogen are emitted into the atmosphere during the burning of oil and coal in power stations and are also present in automobile exhaust fumes. They are the main cause of air pollution in major cities and near power stations burning fossil fuels. They contribute to acid rain and photochemical smog (see Unit18).

You will be surprised to note that nitric oxide (NO), in spite of its reactive and harmful nature occurs in biological systems in traces. It acts as a neurotransmitter and plays a significant role in controlling blood pressure by relaxing blood vessels. It also provides protection from bacterial infections.

13.3.6.1 Nitric acid

Nitric acid is the most important oxoacid formed by nitrogen. It is one of the major industrial chemicals and is widely used. Nitric acid is manufactured by the catalytic oxidation of ammonia in what is known as OSTWALD PROCESS which can be represented by the sequence of reactions shown below :

$$4NH_3(g) + 5O_2(g) \xrightarrow[\text{Catalyst}]{\text{Pt / Rh}} 4NO(g) + 6H_2O(g)$$

$$2NO(g) + O_2(g) \xrightarrow{1120\ K} 2NO_2(g)$$

$$3NO_2(g) + H_2O(l) \rightarrow 2\,HNO_3(aq) + NO(g)$$

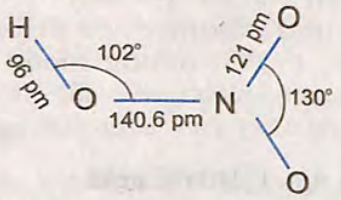
Ammonia is mixed with air and the mixture containing ~ 10% ammonia is passed through a metal gauze made of 90% platinum and 10% rhodium at a temperature of 500K and 9×10^5 Pa (9 bar) pressure. The product mixture containing nitrogen monoxide is cooled below 420K when the unreacted oxygen in the air reacts with NO to give NO_2. The final stage involves the absorption of NO_2 in water to give nitric acid and NO gas, which is recycled. The aqueous nitric acid obtained by this method can be concentrated by distillation to ~68.5% by weight. Further concentration to 98% acid can be achieved by dehydration with concentrated sulphuric acid.

In the laboratory, nitric acid can be prepared by heating $NaNO_3$ or KNO_3 with concentrated sulphuric acid in a glass retort.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

Anhydrous nitric acid can be obtained by distillation of concentrated aqueous nitric acid with P_4O_{10}. It is a colourless liquid with melting and boiling points of 231.4 K and 355.6 K respectively. Its density at 298 K is 1.504 g cm^{-3}. Laboratory grade nitric acid contains 68% of the acid and has a specific gravity of 1.504.

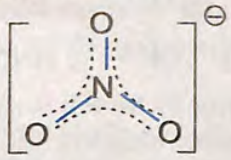
In the gaseous state, HNO_3 exists as planar molecules with the structure shown below.

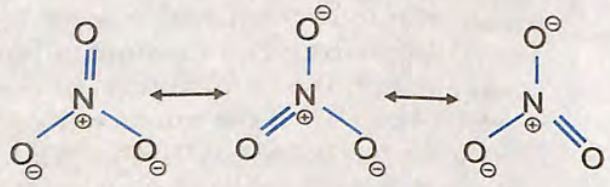


In aqueous solution, nitric acid is a strong acid and dissociates to give hydronium and nitrate ions. Neutralization of the acid with the appropriate alkalies yields nitrates, the salts of nitric acid.

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$

The nitrate ion, NO_3^-, is isoelectronic with the carbonate ion, CO_3^{2-}, and likewise planar. The nitrate ion can be represented by the resonance structures shown below :





Concentrated nitric acid is a strong oxidizing agent and attacks most metals except noble metals such as gold and platinum. Some metals (e.g., Cr, Fe, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film on the surface. The products of reduction depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation. The principal product is nitric oxide (NO), when dilute nitric acid is used and nitrogen dioxide (NO_2), when concentrated HNO_3 is used.

$$3Cu + 8\,HNO_3\ (\text{dilute}) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3\ (\text{conc.}) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2\,H_2O$$

Zinc reacts with dilute nitric acid to give ammonium nitrate :

$$4Zn + 10HNO_3 \rightarrow 4\,Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Concentrated nitric acid also oxidizes nonmetals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to H_2SO_3 and H_2SO_4 and phosphorus to phosphoric acid. Here nitric acid is reduced to nitrogen dioxide (NO_2).

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10\,NO_2 + 4H_2O$$

$$C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$$

$$1/8\,S_8 + 6HNO_3\ (\text{Conc.}) \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

$$1/4\,P_4 + 5HNO_3\ (\text{Conc.}) \rightarrow H_3PO_4 + 5\,NO_2 + H_2O$$

The familiar brown-ring test for nitrates depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown coloured complex. The test is usually carried out by adding dilute ferrous sulphate to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube so that a separate layer is formed. A brown ring at the interface between the solution and sulphuric acid indicates the presence of nitrate ion in solution.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O \quad (\text{brown})$$

Uses of Nitric Acid

The major use of nitric acid is in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene, and other organic nitro compounds. Another major use is in the PICKLING OF STAINLESS STEEL and etching of metals and as an oxidizer in rocket fuels.

13.4 OXYGEN

The electronic configuration of oxygen in its ground state is $1s^2\ 2s^2\ 2p^4$. There are three

naturally occurring isotopes of oxygen, $^{16}_{8}O$(99.762%), $^{17}_{8}O$(0.038%) and $^{18}_{8}O$(0.200%). Like hydrogen, oxygen exists in the elemental form as a diatomic molecule (O_2). **Dioxygen** (O_2) is unique among diatomic molecules. It contains an even number of electrons (16) but two of them are unpaired. Dioxygen is, therefore, paramagnetic. The properties of atomic and molecular oxygen are given in Table 13.4. Oxygen has two allotropes dioxygen (O_2) and trioxygen (O_3), which is called **ozone**.

13.4.1 Occurrence

Just as hydrogen is the most abundant element in the cosmos, oxygen is the most abundant element on earth. Oxygen constitutes nearly 50% by weight of the crust of the earth, water bodies and the atmosphere. In the earth's crust, oxygen occurs in the combined state, mainly in the form of silicates, carbonates and oxides of metals. Water consists of 88.8% oxygen by weight. Dioxygen makes up about 23.2% by weight of the atmosphere.

13.4.2 Preparation

In the laboratory, dioxygen is obtained by the thermal decomposition of oxygen-rich compounds such as $KMnO_4$ or $KClO_3$. The thermal decomposition of $KClO_3$ requires a temperature of 670-720 K. The temperature can be lowered to ~420 K by the use of MnO_2 as a catalyst:

$$2KClO_3(s) \xrightarrow[MnO_2]{heat} 3O_2(g) + 2KCl(s)$$

Another method to prepare dioxygen in the laboratory is by the reaction of water with sodium peroxide :

$$2Na_2O_2(s) + 2H_2O(1) \rightarrow O_2(g) + 4NaOH(aq)$$

Electrolysis of water produces both dihydrogen and dioxygen in a pure state. The most economical method of production of dioxygen on an industrial scale is the fractional distillation of liquid air. In this method, dinitrogen (b.p. 77K) is boiled away leaving behind dioxygen (b.p. 90 K). Production of dioxygen in the world is more than 100 million tonnes per year.

13.4.3 Properties and Reactions

Dioxygen is a colourless, tasteless and odourless highly reactive gas. Its solubility in one litre of water at 293 K is ~ 30 cm^3 gas at STP. This small amount of dissolved dioxygen is sufficient to sustain marine and aquatic life and for the destruction of organic wastes in water bodies.

Dioxygen combines with many metals and non-metals to form binary compounds of oxygen known as OXIDES. The bond dissociation energy of O_2 is high (compared to that of H_2) and hence the reactions of dioxygen require initiation by external heating. Many of these reactions are highly exothermic and the heat liberated is sufficient to sustain the reactions e.g., combustion of charcoal. Most metals (except some of the less active ones such as gold and platinum and most non-metals (with the exception of noble gases) react with dioxygen directly. Some typical reactions of dioxygen are summarized in Fig.13.9.

13.4.4 Uses of Dioxygen

One of the major uses of dioxygen is in making steel and in metal fabrication where it functions as an aid to combustion. Another important use is in the production of oxygen-containing organic chemicals (e.g., ethylene oxide from ethene). Dioxygen is essential for life support systems (e.g., in hospitals, in underwater diving). Liquid dioxygen is used as an oxidizer in rockets for space exploration and in the launching of satellites. It is used on a large scale for the production of TiO_2 and synthesis gas ($CO + H_2$).

Table 13.4 Atomic and Molecular Properties of Oxygen

Atomic Properties		Molecular Properties	
Ionization enthalpy(kJ mol^{-1})	1310	Melting point (K)	54.4
Electron gain enthalpy(kJ mol^{-1})	-140	Boiling point (K)	90.2
Electronegativity	3.5	Density (g/cm^3) at STP	1.429
Atomic radius (pm)	73	Bond length (pm)	120.7
Ionic radius (O^{2-}) (pm)	140	Bond enthalpy (kJ mol^{-1})	493.4

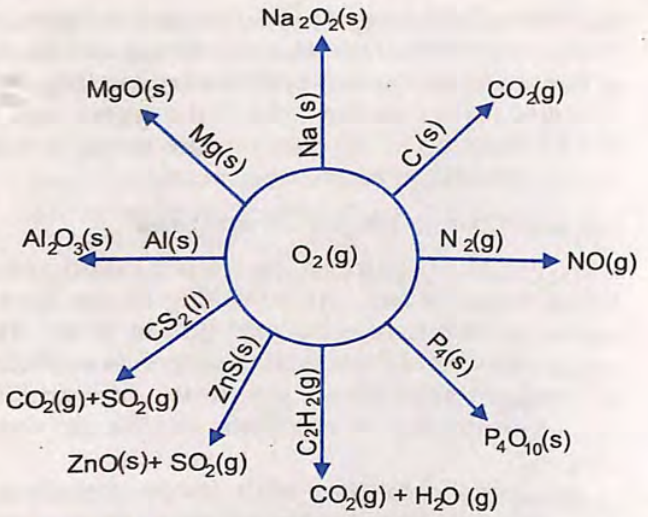


Fig.13.9 *Some typical reactions of dioxygen*

Dioxygen is used for sewage treatment, river revival and paper pulp bleaching.

13.4.5 Simple Oxides

As mentioned earlier, oxygen forms compounds with most elements of the Periodic Table. Many elements form more than one compound with oxygen. In their properties and with regard to nature of bonding, they vary widely. They form both ionic and covalent compounds. A useful classification of the oxides is based on acid-base characteristics. An oxide that combines with water to give an acid is termed as an ACIDIC OXIDE; an oxide that gives a base in water is known as a BASIC OXIDE. An example for each type of oxide is shown below :

$P_4O_{10}(s) + 6\,H_2O(1) \rightarrow 4H_3PO_4(aq)$

$Na_2O(s) + H_2O(1) \rightarrow 2NaOH(aq)$

As a general rule, non-metal oxides are acidic whilst metal oxides are basic. Some oxides are of an intermediate nature; they react with both acids and alkalies and are called AMPHOTERIC OXIDES. These are generally formed by elements that are on the borderline between metals and non-metals (located in the centre of the Periodic Table).

$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$

$Al_2O_3(s)+6NaOH(aq)+3H_2O(1) \rightarrow 2Na_3[Al(OH)_6](aq)$

It may be noted that when we consider the oxides of elements in a given period, there is a progression from strongly basic through amphoteric to strongly acidic oxides.

Na_2O, MgO	Al_2O_3, GeO_2	P_4O_{10}, SO_3, Cl_2O_7
Basic	Amphoteric	Acidic

Undoubtedly, the most important compound of oxygen is water, whose chemistry you learnt in Unit 11.

Example 13.3

Classify the following into acidic, basic or amphoteric oxides. Write balanced equations for the reactions of the oxides with water, acids or alkalies.
SO_2, ZnO, BaO.

Solution

SO_2 is an acidic oxide. Its reaction with water produces sulphurous acid

$SO_2(g) + H_2O(l) \rightarrow 2H^+(aq) + SO_3^{2-}(aq)$.

BaO is basic. Its reaction with water produces alkaline solution of $Ba(OH)_2$.

$BaO(s) + H_2O(l) \rightleftharpoons Ba(OH)_2(aq)$

ZnO is amphoteric. It reacts with an acid to liberate hydrogen and also dissolves in alkali to give $[Zn(OH)_4]^{2-}$ ion.

$ZnO(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2O(l)$

$ZnO(s) + 2OH^-(aq) + H_2O(l) \rightarrow [Zn(OH)_4]^{2-}(aq)$.

13.4.6 Ozone

In addition to the diatomic molecule, O_2, elemental oxygen exists as a triatomic species. O_3, known as ozone. Ozone is a pale blue gas with a characteristic pungent odour. It condenses to a deep blue liquid (b.p. 161.2 K) and to a violet-black solid (m.p. 80.6 K). Ozone is formed when energy is supplied to dioxygen in the form of UV radiation or silent electric discharge.

$3O_2(g) \rightleftharpoons 2O_3(g)$; $\Delta H_{298} = 142.7$ kJ mol^{-1}

The ozone molecule has an angular structure. Both the oxygen-oxygen bonds are of equal length (128 pm). This distance is intermediate between that of a O-O single bond (148 pm) and that of a O = O double bond (110 pm). The bonding in ozone is best described as a resonance hybrid (Unit 6).

In contrast to dioxygen which is paramagnetic, ozone is diamagnetic. Ozone is much more reactive than dioxygen. It acts as a powerful oxidizing agent with the liberation of dioxygen.

Two typical reactions are :

$PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$

$2KI(aq) + O_3(g) + H_2O(l) \rightarrow 2KOH(aq) + I_2(aq) + O_2(g)$

The oxidation of potassium iodide by ozone can be conveniently used for the quantitative estimation of ozone.

Ozone is formed in the upper atmosphere by a photochemical reaction involving dioxygen. Ozone absorbs radiation strongly in the ultraviolet region of the spectrum between 220-290 nm and this protects the earth and its inhabitants from the harmful ultraviolet radiation of the sun. Without this protective layer, more ultraviolet radiation will reach the surface of the earth and cause damage to plant and animal life.

In recent years, there is world-wide concern about the depletion of the ozone layer in the stratosphere caused by the presence of chlorofluorocarbons (CFC's). These volatile compounds have been used for some years as aerosol propellants and as refrigerants. Chlorofluorocarbons are long-lived molecules and diffuse into the stratosphere where they are decomposed by ultraviolet radiation to produce chlorine. The chlorine atoms react with ozone; this causes a decrease in the concentration of ozone at a rate faster than its formation from O_2. Another cause of ozone depletion is release of nitrogen oxides (NO_x) into the stratosphere by the supersonic jet aeroplanes. NO molecule can react with ozone to give O_2.

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

Three scientists, P.J. CRUTZEN, M.J. MOLINA and F.S. ROWLAND received the 1995 Nobel Prize in chemistry for their pioneering work in this area. As a result of their work, there is a great awareness all over the world to find alternatives for CFC's and to limit the NO_x emissions into the stratosphere(See Unit 18).

Ozone is used as a disinfectant (for purifying drinking water) and as a bleaching agent. It also finds use as a chemical reagent in organic chemistry.

SUMMARY

Each group in the *p*-block of the Periodic Table is headed by a **non-metal**. Non-metals in contrast to metals have high ionization enthalpies and high electronegativities. Electron sharing to form covalent bonds is a dominant feature of non-metal chemistry. The first member of each non-metal group differs in many respects from the other members of the group on account of its small size, high electronegativity and the ability to form strong p_π- p_π multiple bonds. **Boron** shows metallic characteristics to some extent but it behaves essentially as a non-metal. The availability of only 3 valence electrons ($2s^2$-$2p^1$) for covalent bond formation using four orbitals (2*s*, $2p_x$, $2p_y$ and $2p_z$) leads to the so-called **electron deficiency** in boron compounds. This deficiency makes them good electron acceptors and thus boron compounds behave as **Lewis acids.** Boron forms an extensive series of covalent molecular compounds with hydrogen known as **boranes**, the simplest of which is **diborane**, B_2H_6. Diborane contains two bridging hydrogen atoms between two boron atoms; these bridge bonds are considered to be **three-centre two-electron bonds**. Boron forms strongest bonds to oxygen. Two important compounds of boron with oxygen are **boric acid** and **borax**. Boric acid, $B(OH)_3$ is a weak mono basic acid; it acts as a **Lewis acid** by accepting electrons from a hydroxyl ion. **Carbon** is a typical non-metal forming covalent bonds in the vast majority of its compounds employing all its four valence electrons ($2s^2 2p^2$). It shows the property of **catenation**, the ability to form chains or rings not only with C-C single bonds but also with multiple bonds (C = C or C ≡ C). Elemental carbon provides one of the best examples of **allotropy.** Allotropy is the phenomenon of polymorphism of elements, in other words, existence of the same element in two or more forms. Three important allotropes of carbon are **diamond**, **graphite** and the recently discovered **fullerenes**. Some of the important inorganic compounds of carbon are the **oxides** (carbon monoxide and carbon dioxide), **carbonates** and **cyanides. Nitrogen** forms compounds in all oxidation states ranging from –3 to +5. Molecular nitrogen (N_2) is not very reactive because of high N ≡ N

bond strength. At elevated temperature it combines with metals to form nitrides. Reaction of dinitrogen with dihydrogen (**Haber process**) is the basis for the manufacture of **ammonia**, which is the starting material for the production of nitrogenous fertilizers.

The oxides of nitrogen (N_2O, NO, NO_2, N_2O_4 and N_2O_5) illustrate the concept of resonance and multiple bonding. NO and NO_2 are intermediates in the manufacture of nitric acid by the oxidation of ammonia. **Nitric acid** is an important industrial chemical. It is a strong acid in water and is a powerful oxidizing agent. Metals dissolve in nitric acid with the reduction of the nitrate ion to NO or NO_2. **Oxygen** is the most abundant element on earth. Elemental oxygen (O_2) combines with many metals to form binary compounds known as **oxides**. As a general rule, non-metal oxides are **acidic** whereas metal oxides are **basic**. **Ozone** (O_3) is an allotrope of oxygen. It has an angular structure. It is diamagnetic in contrast to the paramagnetic O_2. It is a more powerful oxidizing agent than O_2.

EXERCISES

13.1 Write balanced equations for the reaction of elemental boron with elemental chlorine, oxygen and nitrogen at high temperature.

13.2 Why are boron halides and diborane referred to as "electron deficient compounds?

13.3 Write the structure of diborane and explain the nature of bonding in it.

13.4 What happens when a borax solution is acidified ? Write a balanced equation for the reaction.

13.5 Describe what happens when boric acid is heated.

13.6 Describe briefly how elemental boron can be prepared.

13.7 Describe the shapes of BF_3 and BH_4^-. What type of hybridization can we assign to boron in each of these compounds?

13.8 Why do boron halides form "addition compounds" with amines?

13.9 By means of a balanced chemical equation show how $B(OH)_3$ behaves as an acid in water.

13.10 Write balanced equations for the following reactions:
(a) Combustion of C_4H_{10} in a limited supply of oxygen to form carbon monoxide and water.
(b) The reaction of calcium carbide with water to form acetylene.
(c) The preparation of calcium cyanamide from calcium carbide and nitrogen
(d) Formation of hydrogen cyanide from methane and ammonia.

13.11 Write resonance structures for CO_3^{2-} and HCO_3^-.

13.12 What is the oxidation state of carbon in each of the following compounds ?
(a) CO (b) HCN (c) H_2CO_3 (d) CaC_2

13.13 What is dry ice? Why is it so called?

13.14 What is the state of hybridization of carbon in
(a) CO_3^{2-} (b) HCN (c) diamond (d) graphite

13.15 Explain the differences in the properties of diamond and graphite on the basis of their structures.

13.16 What are fullerenes? How are they prepared ?

13.17 Give examples of compounds in which nitrogen exhibits oxidation states of –3, +3 and +5.

13.18 Discuss the conditions required in the Haber process for the manufacture of ammonia.

13.19 How is dinitrogen prepared in the laboratory ?

13.20 Write the products of the following reactions (give balanced equations)
$Mg_3N_2 + H_2O \longrightarrow$
$I_2 + HNO_3$ (concentrated) $\longrightarrow$
$Cu + HNO_3$ (concentrated) $\longrightarrow$
$Li + N_2 \longrightarrow$
$HNO_3 + P_4O_{10} \longrightarrow$

13.21 How would you prepare a sample of deuterated ammonia, ND_3?

13.22 Illustrate how nitrogen compounds provide good examples of *multiple bonding* and *resonance*.

13.23 Determine the oxidation number of nitrogen in
(a) N_2O, (b) NO_2 (c) HNO_3 (d) NH_3

13.24 Write the resonance Lewis structures for N_2O, NO_2 and NO_3^-.

13.25 Illustrate how a metal such as copper can give different products with nitric acid. Give balanced equations.

13.26 Write balanced equation(s) for the manufacture of nitric acid by the oxidation of ammonia.

13.27 Describe the uses of ammonia and nitric acid

13.28 What is the shape of ozone molecule? Write Lewis dot structure(s) for ozone molecule and explain why O-O distances in ozone are equal.

13.29 What is the importance of ozone for plant and animal life on earth?

13.30 Classify the following compounds into acidic, basic and amphoteric oxides:
SrO, SiO_2, Al_2O_3, N_2O_5, SO_2, P_4O_6, Cl_2O_7. Write balanced equations for the reaction of each of these compounds with water, a base or an acid as the case may be.

UNIT 14

ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES

Objectives

After studying this Unit, you will be able to

- understand reasons for tetravalency of carbon and shapes of organic molecules.
- know various ways of representing structures of organic molecules.
- name organic compounds and also derive their structures from a given name.
- understand effects of electronic displacements in covalent bond, influencing structure and reactivity of organic compounds.
- understand organic reactions and their common types.

In Unit 13 you learnt that carbon forms different types of compounds. This is possible because it forms covalent bonds to itself and other elements like hydrogen, oxygen, nitrogen, sulphur, phosphorous and halogens in a variety of ways. The resulting compounds are widely distributed in nature and they play an important role in our daily lives. The branch of chemistry dealing with these compounds is called 'organic chemistry'. In this unit some of the basic principles required for the understanding of the formation and properties of organic compounds will be discussed.

ORIGIN OF ORGANIC CHEMISTRY

In the earlier period of development of chemistry, compounds were classified into two types: organic and inorganic. While the former were taken to be derived from 'living matter' the latter were taken to come from non-living matter. There was the mistaken notion that a 'vital force' was essential for the synthesis of organic compounds. The preparation of urea (present in urine) from the inorganic compound ammonium cyanate by Wöhler in 1828 effectively destroyed the myth of organic compounds being associated with a 'vital force'.

$$\underset{\textit{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\text{heat}} \underset{\textit{Urea}}{NH_2CONH_2}$$

Soon afterwards Herman Kolbé accomplished the synthesis of acetic acid which had been previously obtained from the biological materials. The pioneering work of Lavoisier, Kolbé, Kekulé and Berthelot showed conclusively that organic compounds are essential compounds formed by carbon with itself and other elements and that they can be synthesized in a laboratory as easily as other 'inorganic compounds'. **The chemistry of hydrocarbons and their derivatives constitutes organic chemistry**. The development

of the electronic theory of covalent bonding ushered organic chemistry into its modern shape.

14.1 TETRAVALENCE OF CARBON: SHAPES OF ORGANIC COMPOUNDS

14.1.1 The Shapes of Carbon Compounds

An important aspect of organic chemistry is the understanding of fundamental concepts of molecular structure. This helps in the understanding and prediction of the properties of organic compounds. It may be recalled that the fundamental concepts of electronic theories of valency and molecular structure have already been discussed in Unit 6. We already know that the tetravalency of carbon and the formation of covalent bonds by it are explained in terms of its electronic configuration and the hybridisation of *s* and *p* orbitals. It may be recalled that formation and the shapes of molecules like methane (CH_4), ethene (C_2H_4), ethyne (C_2H_2) were explained in terms of the use of sp^3, sp^2 and *sp* hybrid orbitals by carbon atoms in the respective molecules. Similarly, the formation of sigma, pi and multiple bonds was explained in terms of these hybridisation schemes. The formation of ethane ($CH_3.CH_3$) having two carbon atoms is easily explained in terms of sp^3 hybrid orbital overlaps as shown in Fig.14.1.

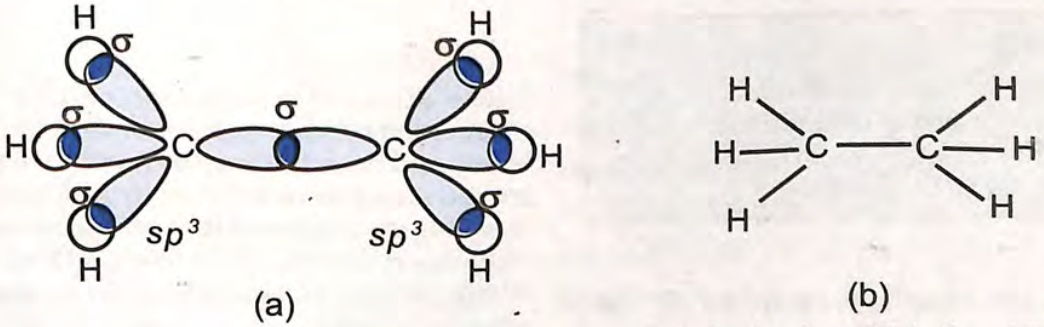


Fig. 14.1 *C_2H_6 formation : (a) orbital overlaps between C (sp^3) and C (sp^3) orbitals and C (sp^3) and H (1s) orbitals (b) Line bond diagram*

Hybridisation influences the bond length and bond enthalphy (strength) in organic compounds. The *sp* hybrid orbital contains more *s* character and hence it is closer to its nucleus and forms shorter and stronger bonds than the sp^3 orbital. The sp^2 hybrid orbital is intermediate between *sp* and sp^3 and, hence, the length and enthalphy of the bonds it forms, is also intermediate between them. The change in hybridisation is also associated with a change in electronegativity. The greater the *s* character of the hybrid orbitals, the greater is the electronegativity. Thus, an *sp* hybridised carbon atom having hybrid orbitals with 50% *s* character is more electronegative than sp^2 or sp^3 hybridised carbon atoms.This relative electronegativity is reflected in several physical and chemical properties of the molecules concerned, about which you will learn in later Units.

14.1.2 Some Characteristic Features of π Bonds

In a π (pi) bond formation parallel orientation of the two *p* orbitals on adjacent atoms is necessary for a proper sideways overlap. Thus, in $H_2C{=}CH_2$ molecule all the atoms must be in the same plane. The *p* orbitals should be parallel mutually and both perpendicular to the plane of the molecule. Rotation of one CH_2 fragment with respect to other interferes with maximum overlap of the *p* orbitals and, therefore, such rotation of carbon-carbon double bond (C=C) is restricted. Consequently, a disubstituted ethene like $C_2H_2Cl_2$ can exist in two forms (I and II) shown below because of the restriction of rotation around the C=C bond. In I, called the *cis* form, the Cl atoms are on the same side while in II - the *trans* form, the Cl atoms are on the opposite sides.

(I) cis form of $C_2H_2Cl_2$ *(II) trans form of $C_2H_2Cl_2$*

The electron charge cloud of the π bond is placed above and below the plane of bonding atoms. This results in the electrons being easily available to attacking (oxidizing) reagents. It is for this reason, that C_2H_4 readily reacts with oxidising reagents like potassium permanganate or potassium dichromate at ordinary temperature, whereas C_2H_6 (which has only σ electrons) is totally unaffected by these reagents at normal temperature. In general, π bonds provide the most reactive centres in unsaturated molecules.

It may, however, be noted that rotation of one CH_3 fragment against another in a C_2H_6 molecule does not affect the overlap in a sigma bond. Consequently, free rotation around a σ bond is permissible. The carbon-carbon σ bond rotations also result in different arrangement of atoms in space giving different interconverting forms of the molecule known as conformations about which you will learn more in Unit 15.

Example 14.1

How many σ and π bonds are present in each of the following molecules?
(a) $HC\equiv CCH=CHCH_3$ (b) $CH_2=C=CHCH_3$

Solution

(a) σ_{C-C}: 4; σ_{C-H}: 6; $\pi_{C=C}$: 1; $\pi C\equiv C$: 2
(b) σ_{C-C}: 3; σ_{C-H}: 6; $\pi_{C=C}$: 2.

Example 14.2

What is the type of hybridisation of each carbon in the following compounds?
(a) CH_3Cl, (b) $(CH_3)_2CO$, (c) CH_3CN,
(d) $HCONH_2$, (e) $CH_3CH=CHCN$

Solution

(a) sp^3, (b) sp^3, sp^2, (c) sp^3, sp, (d) sp^2, (e) sp^3, sp^2, sp^2, sp

Example 14.3

What is the shape of the following compounds?
(a) $H_2C=O$, (b) CH_3F, (c) $HC\equiv N$.

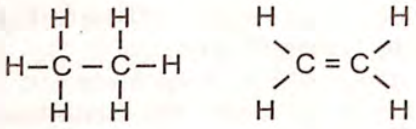
Solution

(a) sp^2 hybridised carbon, Trigonal planar; (b) sp^3 hybridised carbon, Tetrahedral; (c) sp hybridised carbon, Linear.

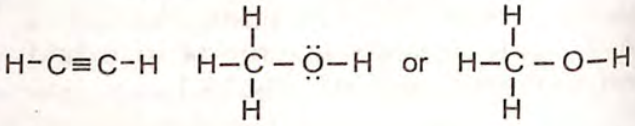
14.2 STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS

14.2.1 Complete, Condensed and Bond-line Structural Formulae

The structures of organic compounds are represented in several ways. The *Lewis structure* is one of the ways. The Lewis structures, however, can be simplified by representing the two-electron covalent bond by a 'stick' (dash, –). Such structural formula focuses on the electrons involved in bond formation, using a dash to represent a single bond, double dash for double bond and triple dash for triple bond. The lone-pairs of electrons on heteroatoms (*e.g.*, oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown. Thus, ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2) and methanol (CH_3OH) can be represented by the following structural formulae. Such structural representations are called *complete structural formulae*.



Ethane *Ethene*



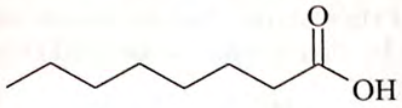
Ethyne *Methanol*

These structural formulae can be further abbreviated by omitting some or all of the covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a *condensed structural formula*. Thus, ethane, ethene, ethyne and methanol can be written as:

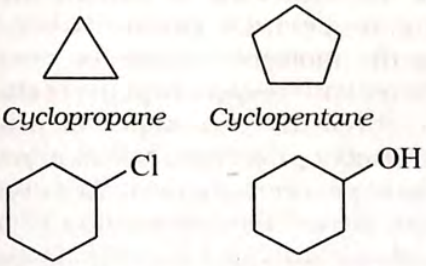
CH_3CH_3 or C_2H_6	$H_2C=CH_2$ or C_2H_4	$HC\equiv CH$ or C_2H_2	CH_3OH
Ethane	*Ethene*	*Ethyne*	*Methanol*

Similarly, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH$ can be further condensed to $CH_3(CH_2)_6COOH$. For further simplification, organic chemists use another way of representing the structures, which uses only the lines. In this *bond-line structural* representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are

drawn in zig-zag fashion. The only atoms specifically written are those that are neither carbon nor hydrogen bound to carbon. The termini denote methyl ($-CH_3$) groups (unless indicated otherwise by a functional group), while the line junctions denote carbon atoms bonded to appropriate number of hydrogens required to satisfy the valency of the carbon atoms. Thus, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH$ can be represented in bond-line formula as:



There are many organic compounds in which carbon atoms are not joined in chain but are joined in rings. A compound containing one or more rings is called a *cyclic compound*, which is represented by drawing the appropriate ring (polygon) without showing the carbon and hydrogen atoms. The corner of polygon represents a carbon atom and the sides of the polygon denote a carbon-carbon bond. If an atom or group of atoms other than hydrogen is attached to carbon, then that atom or group of atoms, is shown in the structure. Examples of cyclic compounds are given below.

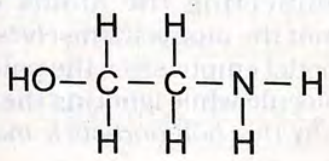


Example 14.4

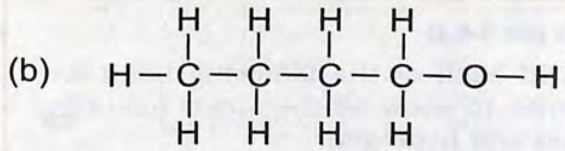
Expand each of the following condensed formulae into their complete structural formulae. (a) $HOCH_2CH_2NH_2$, (b) $CH_3(CH_2)_3OH$, (c) $CH_3CH_2COCH_2CH_3$ (d) $CH_3CH{=}CH(CH_2)_3CH_3$

Solution

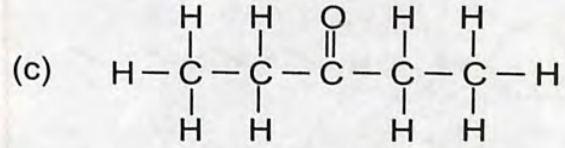
(a)



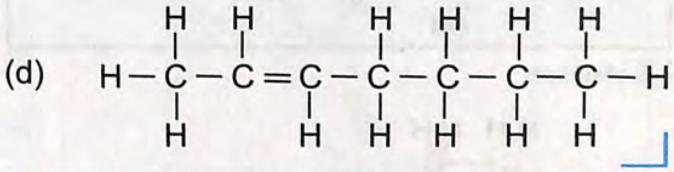
(b)



(c)



(d)



Example 14.5

For each of the following compounds, write a more condensed formula and also their bond-line formula.

(a) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$

(b) $CH_3CH_2CH_2CH_2CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2\underset{\displaystyle H}{\underset{|}{C}}{=}O$

(c) $HOCH_2CH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

(d) $N{\equiv}C{-}\underset{\displaystyle CN}{\underset{|}{C}}H{-}C{\equiv}N$

Solution

Condensed formula

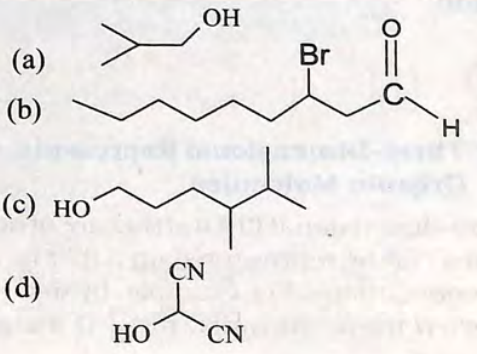
(a) $(CH_3)_2CHCH_2OH$

(b) $CH_3(CH_2)_5CHBrCH_2CHO$

(c) $HO(CH_2)_3CHCH_3CH(CH_3)_2$

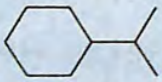
(d) $HOCH(CN)_2$

Bond-line formula

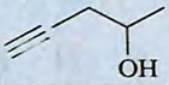


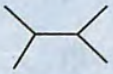
Example 14.6

Expand each of the following bond-line formulae to show all the atoms including carbon and hydrogen.

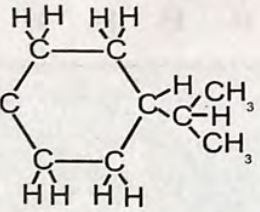
a) 

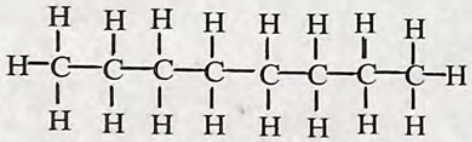
b)

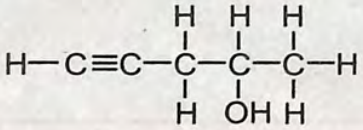
c) 

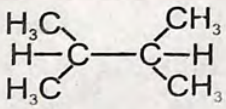
d) 

Solution

(a) 

(b) 

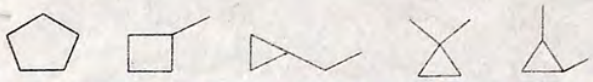
(c) 

(d) 

Example 14.7

Draw polygon formulae for the molecular formula C_5H_{10}.

Solution



14.2.2 Three-Dimensional Representation of Organic Molecules

The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. For example, by using *solid* and *dashed wedge* formula, the 3-D image of a molecule from a two-dimensional picture can be perceived. In these formulae the solid-wedge is used to indicate a bond projecting from the plane of paper towards the observer and the dashed-wedge is used to depict the bond going away from the plane of paper. The bonds lying in plane of the paper are depicted using a normal line. As shown in Fig. 14.2 for CH_4, the two carbon-hydrogen bonds shown by normal lines are in plane of the paper, while the carbon-hydrogen bond shown with a solid wedge is intended to be in front of this plane. The hydrogen connected to carbon by dashed line is behind this plane.

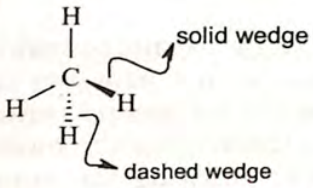


Fig. 14.2 Wedge-and-dash representation of CH_4

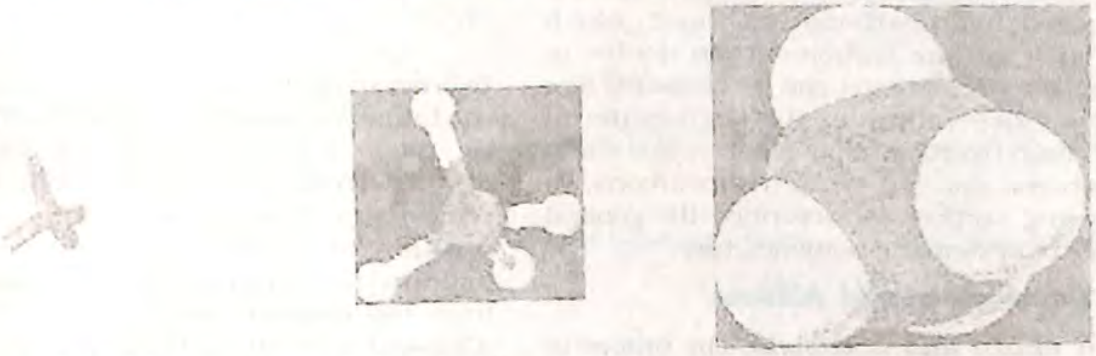
14.2.3 Projection Formulae

In organic molecules, the 3-D arrangement of atoms in space can be represented in plane by *projection formulae*. These formulae are obtained by actually projecting the 3-D model of molecule using a ray of light. Then the two-dimensional image of the molecule is drawn on paper according to certain conventions. While projecting the molecule it may be oriented in different ways with respect to plane of the paper. There are three different types of projection formulae: *Fischer projection*, *Newman projection* and *sawhorse projection formulae*. Details of these representations will be discussed in Unit 15.

MOLECULAR MODELS

Molecular models are physical devices that are used for a better visualisation and perception of three-dimensional shapes of organic molecules. These are made of wood, plastic or metal and are commercially available. Commonly three types of molecular models are used: (1) *Framework model*, (2) *Ball-and-stick model*, and (3) *Space filling model*. In the *framework model* only the bonds connecting the atoms of a molecule and not the atoms themselves are shown. This model emphasizes the pattern of bonds of molecule while ignoring the size of the atoms. In the *ball-and-stick model*,

both the atoms and the bonds are shown. Balls represent atoms and a stick denotes a bond. Unsaturated compounds containing C=C (e.g., ethene) can best be represented by using springs in place of sticks. These models are referred to as *ball-and-spring model*. The *space-filling model* emphasises the relative size of each atom based on its van der Waals radius. Bonds are not shown in this model. It conveys the volume occupied by each atom in the molecule. In addition to these models, computer graphics can also be used for molecular modeling.



Framework model *Ball and stick model* *Space filling model*

14.3 NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming them has been developed and is known as the **IUPAC (International Union of Pure and Applied Chemistry)** system of nomenclature. In this systematic nomenclature, the names are correlated with the structure such that the reader or listener can deduce the structure from the name.

Before the IUPAC system of nomenclature, however, organic compounds were assigned names based on their origin or certain properties. For instance, citric acid is named so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is *formica*. These names are traditional and are known as *trivial* or *common names*. Common names are given even today. For example, a common name Buckminsterfullerene has been given to the newly discovered C_{60} cluster (a form of carbon) noting its structural similarity to the geodesic domes popularised by the famous architect R. Buckminster Fuller. Common names are useful and in many cases indispensable, particularly when the alternative systematic names are lengthy and complicated. The common names of some organic compounds are given in Table 14.1.

14.3.1 The IUPAC System of Nomenclature

A systematic name of an organic compound is generally derived by first identifying and naming a parent structure, which is commonly the parent hydrocarbon. By further using prefixes, infixes and suffixes, the parent name can be

Table 14.1 Common or Trivial Names of Some Organic Compounds

Compound	Common name	Compound	Common name
CH_4	Methane	$CHCl_3$	Chloroform
$H_3CCH_2CH_2CH_3$	*n*-Butane	CH_3COOH	Acetic acid
$(H_3C)_2CHCH_3$	Isobutane	C_6H_6	Benzene
$(H_3C)_4C$	Neo-pentane	$C_6H_5OCH_3$	Anisole
$H_3CCH_2CH_2OH$	*n*-Propyl alcohol	$C_6H_5NH_2$	Aniline
HCHO	Formaldehyde	$C_6H_5COCH_3$	Acetophenone
$(H_3C)_2CO$	Acetone	$CH_3OCH_2CH_3$	Ethyl methyl ether

modified to obtain the actual name. Compounds containing carbon and hydrogen only are called hydrocarbons. A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds. The systematic IUPAC name for such compounds is *alkane*. Paraffin (Latin: little affinity) was the earlier name given to these compounds. Unsaturated hydrocarbons are those, which contain at least one carbon-carbon double or triple bond. Hydrocarbons can be classified into three types depending on their structure: (i) straight chain hydrocarbons, (ii) branched chain hydrocarbons, and (iii) cyclic hydrocarbons. In the following section are described the general principles of systematic nomenclature.

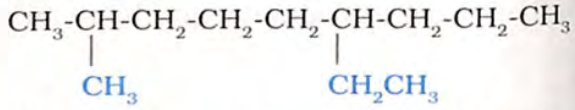
14.3.2 Nomenclature of Alkanes

Straight chain hydrocarbons: The names of such compounds are based on their straight chain structure, and end with '-ane' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH_4 to C_4H_{10}, where the prefixes are derived from trivial names). The IUPAC names of some straight chain saturated hydrocarbons are given in Table 14.2. The alkanes in Table 14.2 differ from each other by merely the number of $-CH_2$ groups in the chain. Such a family of *compounds in which two successive members differ from each other by a CH_2 group in the chain is called a homologous series.* The individual members of the series are called *homologues*.

Table 14.2 IUPAC Names of Some Unbranched Saturated Hydrocarbons

Name	Molecular formula	Name	Molecular formula
Methane	CH_4	Heptane	C_7H_{16}
Ethane	C_2H_6	Octane	C_8H_{18}
Propane	C_3H_8	Nonane	C_9H_{20}
Butane	C_4H_{10}	Decane	$C_{10}H_{22}$
Pentane	C_5H_{12}	Icosane	$C_{20}H_{42}$
Hexane	C_6H_{14}	Triacontane	$C_{30}H_{62}$

Branched chain hydrocarbons: In branched chain compounds, all the carbon atoms are not present in a linear sequence. Some of them are attached to the chain at one or more points, for example:



In order to name such compounds, the names of the branches called alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. The position of the hydrogen atom removed is indicated by giving it the lowest possible number from the chain terminus. Thus, CH_4 becomes $-CH_3$ and is called *methyl group*. An alkyl group is named by substituting 'yl' for 'ane' in the corresponding alkane. Some alkyl groups are listed in Table 14.3.

Some of the alkyl groups are also written using abbreviation. For example, methyl as Me, ethyl as Et, propyl as Pr and butyl as Bu. The alkyl groups can be branched also. Thus, propyl and butyl groups can have branched structures as shown below. Common branched groups have specific trivial names. For example, the two propyl groups are called propyl group and isopropyl group. The branched butyl groups are called *sec*-butyl, isobutyl and *tert*-butyl group. We also encounter the structural unit, $-CH_2C(CH_3)_3$, which is called neopentyl group.

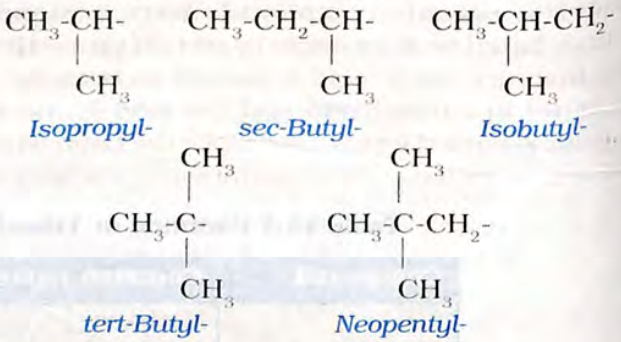
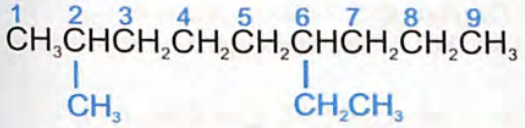


Table 14.3 Some Alkyl Groups

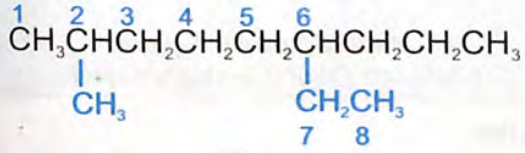
Alkane		Alkyl group	
Molecular formula	Name of alkane	Structural formula	Name of alkyl group
CH_4	Methane	$-CH_3$	Methyl
C_2H_6	Ethane	$-CH_2CH_3$	Ethyl
C_3H_8	Propane	$-CH_2CH_2CH_3$	Propyl
C_4H_{10}	Butane	$-CH_2CH_2CH_2CH_3$	Butyl
$C_{10}H_{22}$	Decane	$-CH_2(CH_2)_8CH_3$	Decyl

Nomenclature of branched chain alkanes: We encounter a number of branched chain alkanes. The rules for naming them are given below.

1. First of all, the longest straight carbon chain in the molecule is identified. In the example given below, the longest chain has nine carbons (I) and it is considered as the *parent* or *root* chain. The parent chain shown in II is not correct as it has only eight carbons.

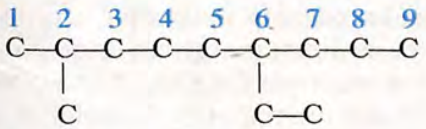


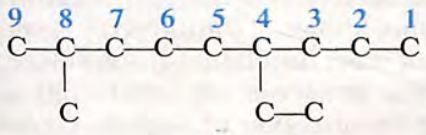
I



II

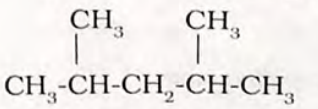
2. The carbon atoms on the parent chain are numbered to identify the parent alkane and the positions of the carbon atoms at which branching takes place by substitution of alkyl groups at these carbons (also called side chain). The numbering is done in such a way that the substituted carbon atoms have the lowest possible numbers. Thus, the numbering in the above example should be from left to right (substituted carbon atoms 2 and 6) and not from right to left (giving carbon atoms 4 and 8).



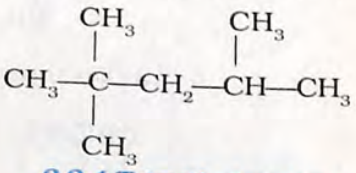


3. The substituted alkyl groups are then prefixed to the name of the parent alkane, the position of the substituents being indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, name for the compound shown above is: 6-Ethyl-2-methylnonane. [note: the numbers are separated from the groups by hyphens and there is no break between methyl and nonane].

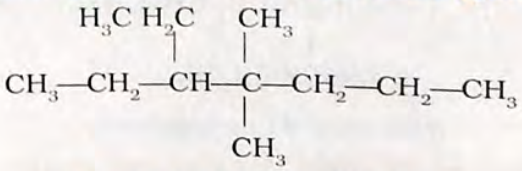
4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta- (for 5), hexa- (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however are not considered. Thus, the following compounds are named as:



2,4-Dimethylpentane

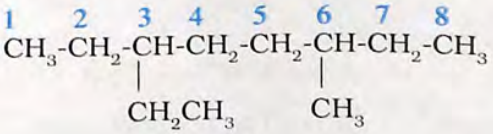


2,2,4-Trimethylpentane

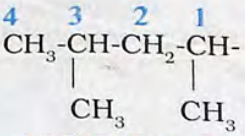


3-Ethyl-4,4-dimethylheptane

5. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing. Thus, the following compound is 3-Ethyl-6-methyloctane and not 6-Ethyl-3-methyloctane.



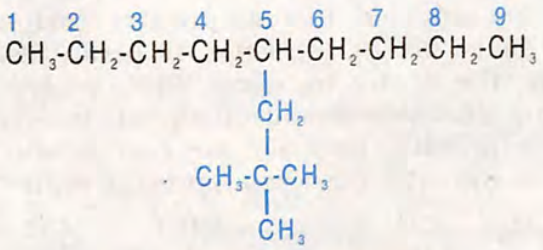
6. The branched alkyl groups can be named by following the above mentioned procedures. However, the carbon atom in the branched alkyl group that attaches to the root alkane is numbered 1 as exemplified below.



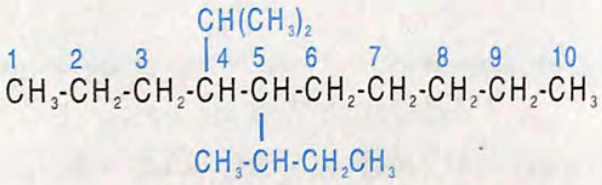
1,3-Dimethylbutyl-

While writing the substituents' name in alphabetical order, the prefixes iso- and neo- are considered to be part of the fundamental name of alkyl group. The prefixes *sec-* and *tert-* are not, however, considered to be the part of the fundamental name. The use of iso and related common prefixes for describing alkyl groups along the longest sequence of carbon atoms as long as these are not further substituted are also

allowed by the IUPAC nomenclature. These points are illustrated by the following examples.



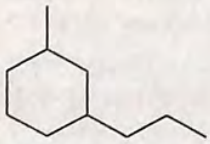
5-(2,2-Dimethylpropyl)nonane



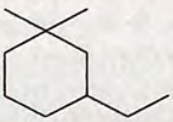
5-sec-Butyl-4-isopropyldecane

Cyclic Compounds: A saturated monocyclic compound is named by prefixing 'cyclo' to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. Names of some cyclic compounds are given below.

Cyclopentane



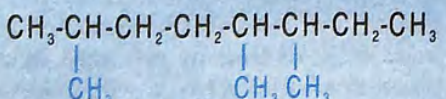
1-Methyl-3-propylcyclohexane



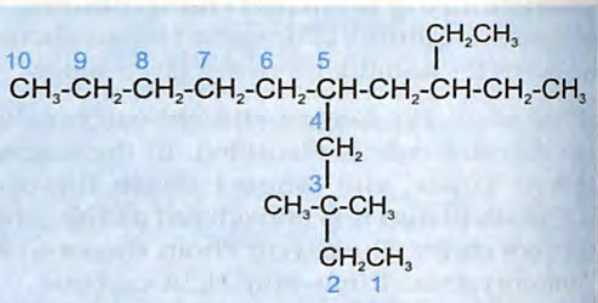
3-Ethyl-1,1-dimethylcyclohexane
(not 1-ethyl-3,3-dimethylcyclohexane)

Example 14.8

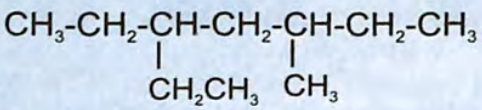
Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parenthesis are incorrect.

(a) 

2,5,6- Trimethyloctane
[and not 3,4,7-Trimethyloctane]

(b) 

5-(2-Ethylbutyl) -3,3-dimethyldecane
[and not 5-(2,2-Dimethylbutyl)-3-ethyldecane]

(c) 

3-Ethyl-5-methylheptane
[and not 5-Ethyl-3-methylheptane]

Solution

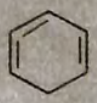
(a) Lowest locant number, 2,5,6 is lower than 3,5,7, (b) greater number of substituents attached to the parent chain, (c) substituents are in equivalent position; lower number is given to the one that comes first in the name according to alphabetical order.

14.3.3 Nomenclature of Organic Compounds Bearing Functional Group(s)

Functional group: A functional group is an atom or group of atoms bonded together in a unique fashion which is usually the site of chemical reactivity in an organic molecule. Compounds having the same functional group undergo similar reactions. For example CH_3OH, CH_3CH_2OH, and $(CH_3)_2CHOH$ all having -OH functional group liberate hydrogen on reaction with sodium metal. Exceptions are known, if the molecule is very large or has two or more functional groups close to one another. The presence of functional groups enables systematisation of organic compounds into different classes. In Table 14.4 are listed examples of some functional groups with their prefixes, suffixes and names of organic compounds bearing them.

Naming of a functionalised organic compound: The systematic name of an organic compound can easily be obtained using Table 14.4. For this purpose the following procedure is adopted. First of all, the functional group present is identified which determines the choice of appropriate suffix. The chain is

Table 14.4 Some Functional Groups (and classes of organic compounds)

Class of Compounds	Functional Group structure	IUPAC group prefix	IUPAC suffix	Example
Alkanes (none)	-	-	-ane	Butane, $CH_3(CH_2)_2CH_3$
Alkenes	>C=C<	-	-ene	But-1-ene, $CH_2=CHCH_2CH_3$
Alkynes	-C≡C-	-	-yne	But-1-yne, $CH{\equiv}CCH_2CH_3$
Arenes	-	-	-	Benzene 
Halides	-X (X=F,Cl,Br,I)	halo-	-	1-Bromobutane $CH_3(CH_2)_2CH_2Br$
Alcohol	-OH	hydroxy-	-ol	Butan-2-ol, $CH_3CH_2CHOHCH_3$
Aldehyde	-CHO	formyl, or oxo	-al	Butanal, $CH_3(CH_2)_2CHO$
Ketone	>C=O	oxo-	-one	Butan-2-one, $CH_3CH_2COCH_3$
Nitrile	-C≡N	cyano	nitrile	Pentanenitrile $CH_3CH_2CH_2CH_2CN$
Ether	-R-O-R-	alkoxy-	-	Ethoxyethane, $CH_3CH_2OCH_2CH_3$
Carboxylic acid	-COOH	carboxy	-oic acid	Butanoic acid, $CH_3(CH_2)_2CO_2H$
Carboxylate ion	$-COO^-$	-	-oate	Sodium butanoate, $CH_3(CH_2)_2CO_2^-\ Na^+$
Ester	-COOR	alkoxycarbonyl	-oate	Methylpropanoate $H_3CCH_2COOCH_3$
Acyl halide	-COX (X=F,Cl.Br,I)	halocarbonyl	-oyl halide	Butanoyl chloride, $CH_3(CH_2)_2COCl$
Amine	$-NH_2$ >NH >N-	amino-	-amine	2-Butanamine $CH_3CHNH_2CH_2CH_3$
Amide	$-CONH_2$, -CONHR, $-CONR_2$	-carbamoyl	-amide	Butanamide, $CH_3(CH_2)_2CONH_2$
Nitro	$-NO_2$	Nitro-	-	1-Nitrobutane, $CH_3(CH_2)_3NO_2$

numbered in such a way that the functional group is attached at the lowest possible number in the chain. By using the suffix as given in Table 14.4, the name of the compound is arrived at.

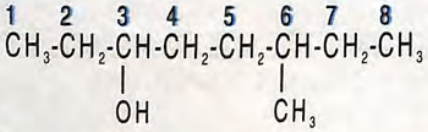
In case of polyfunctional compounds, one of the functional groups is chosen as the *principal functional group* and the compound is then named on that basis. The subordinate functional groups are named as substituents using the appropriate prefixes. The choice of principal functional group is made on the basis of order of preference. The nomenclature priorities, in order of decreasing priority of some functional groups are: -COOH, –COOR, -COCl, (R=alkyl group), $-CONH_2$, -HC=O, -CN, >C=O, -OH, $-NH_2$, >C=C<, -C≡C-. The R or C_6H_5-, OR, Cl, Br, NO_2 etc. are prefix substituents. Thus, a compound containing both an alcohol and a keto group is named as hydroxyalkanone since the keto group is preferred to the hydroxyl group. For example, $HOCH_2(CH_2)_3CH_2COCH_3$ will be named as 7-hydroxyheptan-2-one and not as 2-oxo–hept-7-ol. Similarly, $BrCH_2CH=CH_2$ is named as 3-bromoprop-1-ene and not 1-bromoprop-2-ene.

If more than one functional group of the same type are present, their number is indicated by adding di, tri, etc. before the class suffix. In such cases the full name of the parent alkane is written before the class suffix. For example $CH_2(OH)$-$CH_2(OH)$ is named as ethane –1,2–diol. However, the ending – ne of the parent alkane is dropped in case of compounds having more than one double or triple bond; for example, $CH_2=CH$-$CH=CH_2$ is named as buta–1,3–diene.

Example 14.9

Derive the IUPAC names of the compounds i-iv from their given structures.

(i)



Solution

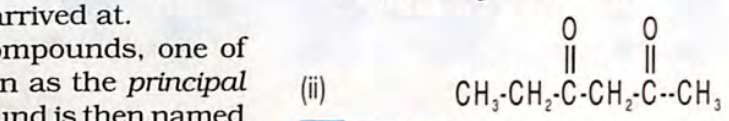
☞ The functional group present is an alcohol (OH). Hence the suffix is '-ol'.

☞ The longest chain containing -OH has eight carbon atoms. Hence the corresponding saturated hydrocarbon is octane.

☞ The -OH is on carbon atom 3. In addition, a methyl group is attached at 6th carbon.

☞ Hence, the systematic name of this compound is: 6-Methyloctan-3-ol.

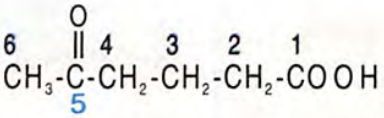
(ii)



Solution

The functional group present is ketone (>C=O), hence suffix '-one'. Presence of two keto groups is indicated by 'di', hence suffix becomes 'dione'. The two keto groups are at carbons 2 and 4. The longest chain contains 6 carbon atoms, hence parent hydrocarbon is hexane. Thus, the systematic name is: hexane-2,4-dione.

(iii)



Solution

Here, two functional groups namely ketone and carboxylic acid are present. The principal functional group is the carboxylic acid group, hence the parent chain will be suffixed with 'oic' acid. The keto group in the chain at carbon 5 is indicated by 'oxo'. The longest chain including the principal functional group has 6 carbon atoms, hence the parent hydrocarbon is hexane. The compound is, therefore, named as: 5-oxohexanoic acid.

(iv)

Solution

The two C=C functional groups are present at carbon atoms 1 and 3, while the C≡C functional group is present at carbon 5. These groups are indicated by suffixes 'diene' and 'yne' respectively. The longest chain containing the functional groups has 6 carbon atoms, hence the parent hydrocarbon is hexane. The name of compound, therefore, is: Hexa-1,3-dien-5-yne.

Example 14.10

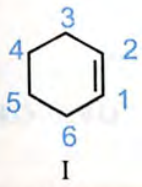
Derive the structure of (i) 2-Chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3- Nitrocyclohexene, (iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxy-heptanal.

Solution

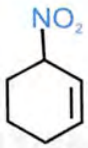
(i) '-hexane' indicates the presence of 6 carbon atoms chain. The functional group chloro is present at carbon 2. Hence, the structure of the compound is: $CH_3CH_2CH_2CH_2CHClCH_3$.

(ii) 'pent' indicates the parent hydrocarbon to contain a 5 carbon atoms chain. 'en' and 'ol' correspond to the functional groups C=C and -OH at carbon atoms 4 and 2 respectively. Thus, the structure is: $CH_2=CHCH_2CH(OH)CH_3$.

(iii) A six membered ring containing a C=C is implied by cyclohexene, which is numbered as shown in I. The prefix 3-nitro means that a nitro group is present on C-3. Thus, complete structural formula of the compound is II:



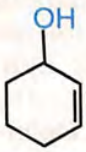
I



II

(iv) A six membered ring is implied by cyclohex-, and 'en' at carbon-2 denotes the presence of a C=C double bond at that carbon (1). '1-ol' means that a -OH group is present at C-1. Thus the structure is as shown in II:

I

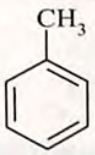


II

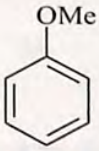
(v) 'heptanal' indicates the compound to be an aldehyde containing 7 carbon atoms in the parent chain. The '6-hydroxy' indicates that -OH group is present at carbon 6. Thus, the structural formula of the compound is: $CH_3CH(OH)CH_2CH_2CH_2CH_2CHO$.

14.3.4 Nomenclature of Substituted Benzene Compounds

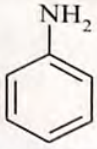
For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word *benzene* as shown in the following examples. However, common names (written in bracket below) of many substituted benzene compounds are also universally used.



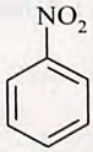
Methylbenzene
(Toluene)



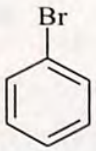
Methoxybenzene
(Anisole)



Aminobenzene
(Aniline)

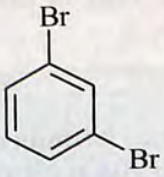


Nitrobenzene



Bromobenzene

If benzene ring is disubstituted, the position of substituents is defined by numbering around the ring such that the substituents are located at the lowest numbers possible. For example, the following compound is named as 1,3-dibromobenzene and not as 1,5-dibromobenzene.



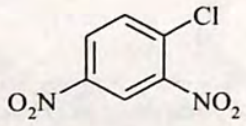
1,3-Dibromobenzene

In the trivial system of nomenclature the terms *ortho* (*o*), *meta* (*m*) and *para* (*p*) are used as prefixes to indicate the relative positions 1,2-; 1,3- and 1,4- respectively. Thus, 1,3-dibromobenzene is named as *m*-dibromobenzene (*meta* is abbreviated as *m*-) and the other isomers of dibromobenzene 1,2- and 1,4-, are named as *ortho* (or just *o*-) and *para* (or just *p*-)-dibromobenzene, respectively.

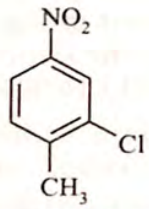
For tri - or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound.

The base compound substituent is numbered 1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents appear in the name in

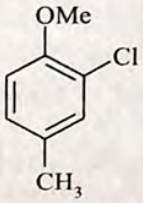
alphabetical order. Some examples are given below.



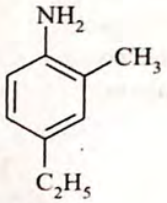
1-Chloro-2,4-dinitrobenzene
(not 4-chloro, 1,3-dinitrobenzene)



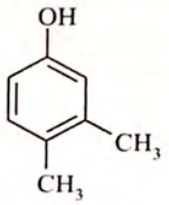
2-Chloro-1-methyl-4-nitrobenzene
(not 4-methyl,5-chloro-nitrobenzene)



2-Chloro-4-methylanisole



4-Ethyl-2-methylaniline



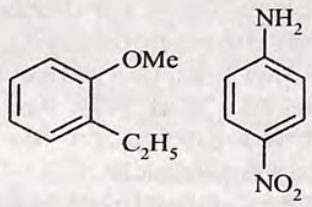
3,4-Dimethylphenol

When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is *phenyl* (C_6H_5-, also abrreviated as Ph).

Example 14.11

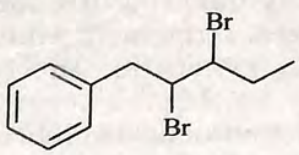
Write the structural formula of :
(a) *o*-Ethylanisole, (b) *p*-Nitroaniline,
(c) 2,3 - dibromo -1 - phenylpentane,
(d) 4-Ethyl-1-fluoro-2-nitrobenzene.

Solution

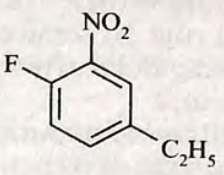


(a)

(b)



(c)



(d)

14.4 CLASSIFICATION OF ORGANIC COMPOUNDS

As mentioned above, carbon atoms bond to each other forming both open chain as well as ring compounds. The chain compounds are called *open-chain* compounds and the ring compounds are called *cyclic* compounds. Further, organic compounds are broadly classified in two major classes: (a) *aliphatic* (b) *aromatic*.

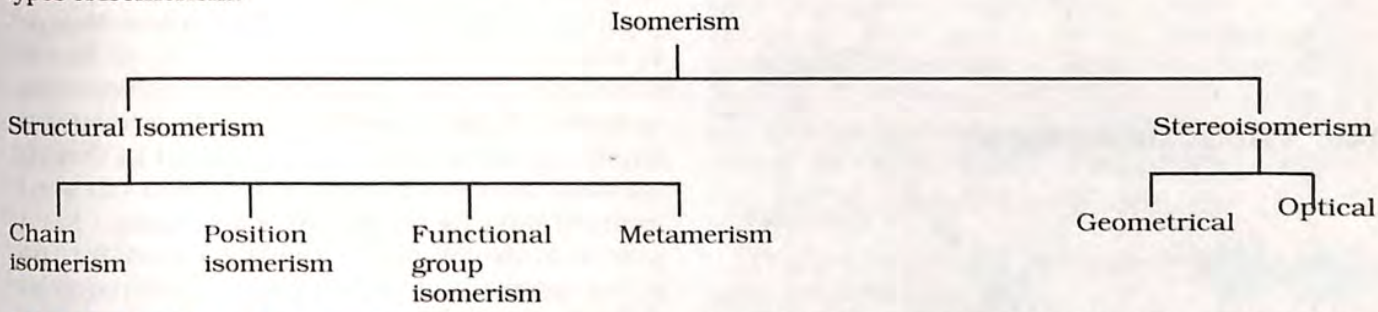
Aliphatic (meaning fatty) compounds include open-chain compounds and those cyclic compounds that resemble open-chain compounds. Open-chain aliphatic compounds are known as *acyclic* while compounds containing ring of carbon atoms are termed as *alicyclic* compounds. In cyclic compounds, there may be one or more rings. Some examples of acyclic (open chain aliphatic) compounds are propane, butene, buta-1,3-diene, hexane, decane etc., while alicyclics (cyclic aliphatic) include compounds such as cyclopropane, cyclobutane, cyclohexane etc. *Aromatic compounds* (originally so named because of their pleasant fragrance) are characterised by an unusual stability called aromatic stability. These include benzene and other related ring compounds.

Organic compounds can also be classified in families on the basis of the functional groups they contain (see Table 14.4). Thus, organic compounds can be categorised into alkanes, alkenes, alkynes, arenes, halides, alcohols, aldehydes, ketones,

carboxylic acids, amines, esters, amides, nitro compounds, nitriles etc.

14.5 ISOMERISM

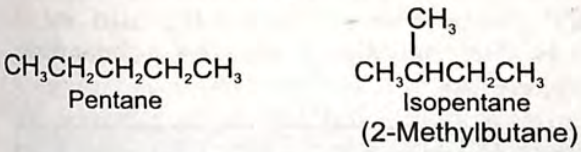
The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as **isomerism**. Such compounds are individually referred to as isomers. The following flow chart shows different types of isomerism.

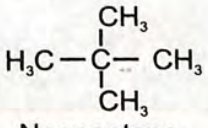


14.5.1 Structural Isomerism

Compounds having the same molecular formula but different structures (manners of linking the atoms) are classified as structural isomers. Some typical examples of different types of structural isomerism are given below.

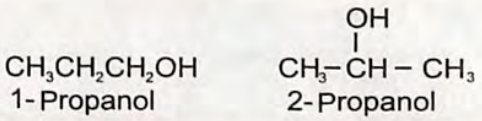
(i) ***Chain isomerism:*** When two or more compounds have similar molecular formula but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, C_5H_{12} represents three compounds:



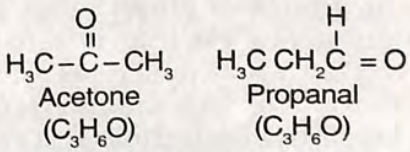


Neopentane
(2,2-Dimethylpropane)

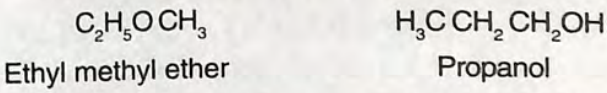
(ii) Position isomerism: When two or more compounds differ in the position of substitutent atom or group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula C_3H_8O represents two alcohols:



(iii) Functional group isomerism: Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed functional group isomerism. For example, the molecular formula C_3H_6O represents an aldehyde and a ketone;



and C_3H_8O represents an ether and an alcohol.



(iv) Metamerism: It arises due to unequal distribution of alkyl groups on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane ($CH_3OC_3H_7$) and ethoxyethane ($C_2H_5OC_2H_5$).

14.5.2 Stereoisomers

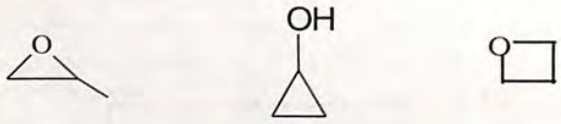
Stereoisomers are compounds that have the same constitution and sequence of covalent bonds but differ in the relative positions of their atoms or groups in space. For example, the *cis-trans* isomerism mentioned in section 14.1.2 is an example of stereoisomerism. The rotation around carbon-carbon bond is prohibited due to π bonding between the two carbon atoms hence geometry of the groups attached to these carbons is fixed in space. This kind of stereoisomerism is known as *geometrical isomerism*. You will learn more about stereoisomerism in Unit 15 and later in Class XII.

Example 14.12

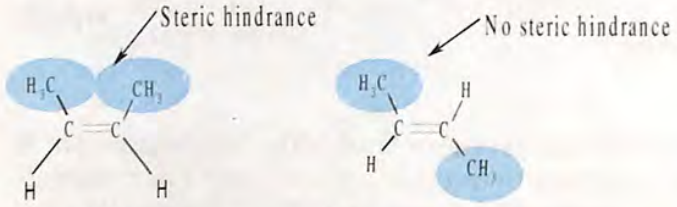
Write structural isomers of molecular formula C_3H_6O.

Solution

CH_3CH_2CHO, $CH_2{=}CHCH_2OH$, CH_3COCH_3,



14.6 STERIC HINDRANCE



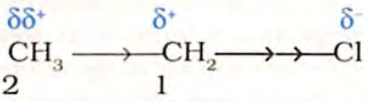
cis-But-2-ene *trans*-But-2-ene

Two atoms or groups of atoms in an organic molecule at a distance less than or equal to the sum of the van der Waals radii repel each other due to spatial crowding. This repulsion is referred to as *steric hindrance* (some time also called as *steric strain* or *van der Waals strain*). Molecules with steric strain are relatively less stable as compared to those having no steric strain. For example, steric hindrance is present in the *cis* isomer of but-2-ene but not in the *trans* isomer as shown below. Steric effects greatly influence the structure and reactivity of organic compounds.

14.7 INDUCTIVE EFFECT

When a covalent bond is formed between atoms of different electronegativity, the bonding electrons are unequally shared and the electron density is more towards that atom of the bond, which has greater electronegativity. Such unequal sharing of electrons results in a *polar covalent bond*. Bond polarity leads to various electronic effects in organic compounds.

Let us consider chloroethane (CH_3CH_2Cl) in which the C-Cl bond is a polar covalent bond. It is polarised in such a way that the carbon – 1 gains some positive charge (δ^+) and the chlorine some negative charge (δ^-). (The fractional electronic charges on the two atoms in polar covalent bond are denoted by symbol δ (delta) and different electron density within a covalent bond by arrow that points from δ^+ to δ^- end of the polar bond).



In turn carbon-1, which has developed partial positive charge (δ^+) draws some electron density towards it from the adjacent C-C bond. Consequently, some positive charge ($\delta\delta^+$) develops on carbon-2 also, where $\delta\delta^+$ symbolises relatively smaller positive charge as compared to that on carbon – 1. In other words, the polar C – Cl bond induces polarity in the adjacent bonds. Such polarisation of one σ-bond caused by the polarisation of adjacent σ-bond is referred to as the **inductive effect**. This effect is passed on to the subsequent bonds also but the effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after four bonds. The inductive effect is related to the ability of substituent (s) to either withdraw or donate electron density to the attached carbon atom. Based on this ability, the substitutents can be classified as *electron-withdrawing* or *electron donating* groups relative to hydrogen. Halogens and many other groups such as nitro (- NO_2), cyano (- CN), carboxy (- COOH), ester (-COOR), aryloxy (-OAr, e.g. – OC_6H_5), etc. are electron-withdrawing groups. On the other hand, the alkyl groups like methyl (- CH_3) and ethyl (-CH_2-CH_3) are usually considered as electron donating groups.

Example 14.13

Which bond is more polar in the following pairs of molecules: (a) H_3C-H, H_3C-Br (b) H_3C-NH_2, H_3C-OH (c) H_3C-OH, H_3C-SH

Solution

(a) C–Br, since Br is more electronegative than H, (b) C–O, (c) C–O

Example 14.14

In which C-C bond of $CH_3CH_2CH_2Br$, the inductive effect is expected to be the least?

Solution

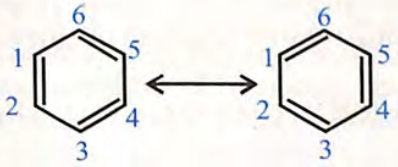
Magnitude of inductive effect diminishes as the number of intervening bonds increases. Hence, the effect is least in C_2-C_3 bond.

14.8 RESONANCE STRUCTURES

There are many organic molecules whose behaviour cannot be explained by a single Lewis structure. An example is that of benzene. Its cyclic structure containing alternating C-C single and C=C double bonds shown below is inadequate for explaining its characteristic properties.

Benzene

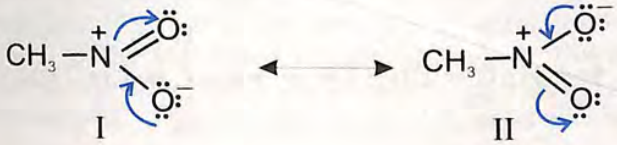
As per the above representation benzene should exhibit two different bond lengths, due to C-C single and C=C double bonds. However, as determined experimentally benzene has a uniform C-C bond distances of 139 pm, a value intermediate between the C-C single and C=C double bonds. Thus, the structure of benzene cannot be represented adequately by the above structure. Further, benzene can be represented equally well by the energetically identical structures I and II.



I II

Therefore, according to the resonance theory (Unit 6) the actual structure of benzene cannot be adequately represented by any of these structures, rather it is a resonance hybrid of the two structures (I and II) called *resonance structures*. The resonance structures (canonical structures or contributing structures) are hypothetical and individually do not represent any real molecule. They contribute to the actual structure in proportion to their stability.

Another example of resonance is provided by nitromethane (CH_3NO_2) which can be represented by two Lewis structures, (I and II). There are two types of N-O bonds in these structures.



I II

However, it is known that the two N-O bonds of nitromethane are of the same length (intermediate between a N-O single bond and a N=O double bond). The actual structure of nitromethane is therefore a resonance hybrid of the two canonical forms I and II.

The energy of actual structure of the molecule (the resonance hybrid) is lower than that of any of the canonical structures. The difference in energy between the actual structure and the lowest energy resonance structure is called the ***resonance stabilisation energy*** or simply the ***resonance energy***. The more the number of important contributing structures, the more is the resonance energy. Resonance is particularly important when the contributing structures are equivalent in energy.

The following rules are applied while writing resonance structures:

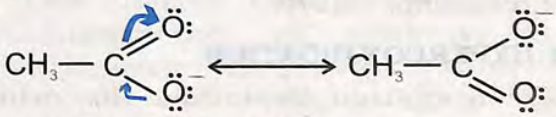
The resonance structures have (i) the same positions of nuclei and (ii) the same number of unpaired electrons. Among the resonance structures, the one which has more number of covalent bonds, less separation of opposite charges, a negative charge if any on more electronegative atom, a positive charge if any on more electropositive atom and more dispersal of charge is more stable than others. (see Unit 6 for details).

Example 14.15

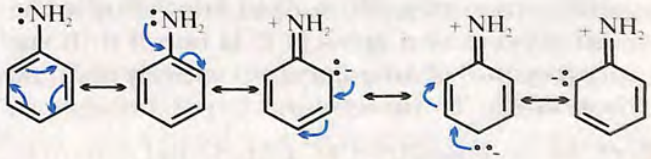
Write resonance structures of, (a) CH_3COO^- and (b) $C_6H_5NH_2$. Show the movement of electrons by curved arrows.

Solution

(a) First, write the structure and put unshared pairs of valence electrons on appropriate atoms. Then draw the arrows one at a time moving the electrons to get the other structures.



(a)

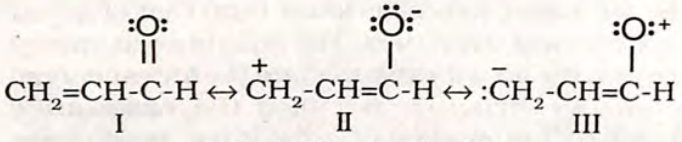


(b)

Example 14.16

Write resonance structures of CH_2=CH-CHO. Indicate relative stability of the contributing structures.

Solution

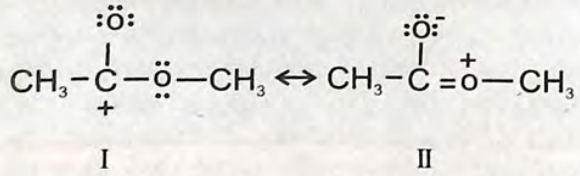


Stability: I > II > III

[I: Most stable, each carbon and oxygen atom has an octet and no carbon or oxygen atom has a charge; II: negative charge on more electronegative atom and positive charge on more electropositive atom; III: least stable as more electronegative oxygen has positive charge and electropositive carbon has negative charge].

Example 14.17

Give reasons why the following two structures I and II cannot be the major contributors to the real structure of CH_3COOCH_3.



Solution

The two structures are less important contributors as they contain charge separation. Additionally, structure I contains a carbon atom with an incomplete octet.

14.9 HYPERCONJUGATION

Hyperconjugation describes the orbital interactions between the π systems and the adjacent σ bonds of the substituent group(s) in organic compounds. This effect arises due to the partial overlap of a sp^3-s (a C-H bond) with the empty p orbital of an adjacent positively charged carbon atom. To understand hyperconjugation effect, let us consider $CH_3\overset{+}{C}H_2$ (ethyl cation) in which the positively charged carbon atom has an empty p orbital. One of the C-H bonds of the methyl group can align in the plane of this empty p orbital and the electrons constituting the C-H bond in plane with this p orbital can then be delocalised into the empty p orbital as depicted in Fig. 14.3.

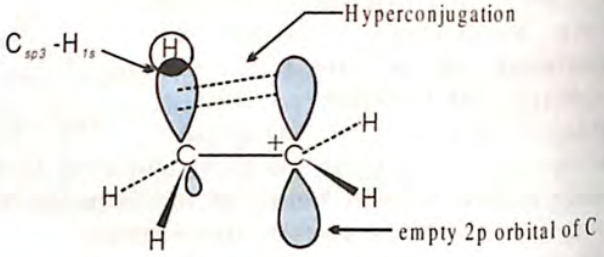
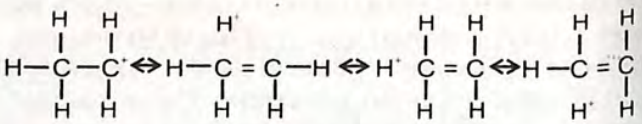


Fig. 14.3 *Orbital diagram showing hyperconjugation in ethyl cation*

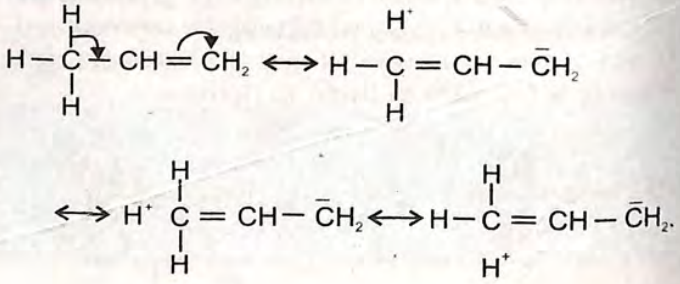
Such interaction between an empty p orbital with the adjacent C-H σ bond is referred to as *hyperconjugation*. This type of overlap stabilises the cation because electron density from the adjacent σ bond helps in dispersing the positive charge. In general, greater the number of alkyl groups attached to a positively charged carbon atom, greater is the hyperconjugation interaction and the stabilisation of the cation. Thus, we have the following relative stability of carbocations:

$$(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

Hyperconjugation is also referred to as no-bond resonance. Such resonance structures of ethyl cation can be shown as follows.



Hyperconjugation is also possible in alkenes and alkylarenes. For example, for propene, it can be shown as follows:



Example 14.18

Explain why $(CH_3)_3C^+$ is more stable than $CH_3CH_2^+$ and CH_3^+ is the least stable cation.

Solution

Hyperconjugation interaction in $(CH_3)_3C^+$ is greater than in $CH_3CH_2^+$ as the $(CH_3)_3C^+$ has nine C-H bonds. In CH_3^+, the C-H bonds lie in the nodal plane of the vacant 2*p* orbital and hence cannot overlap with it. Thus, CH_3^+ lacks hyperconjugative stability.

14.10 ORGANIC REACTIONS AND THEIR CLASSIFICATION

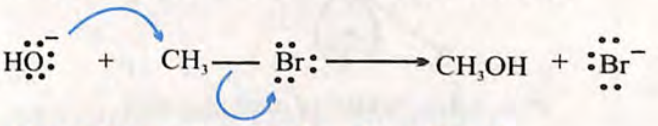
14.10.1 Organic reactions

Consider the following equation.

$$\underset{\text{Substrate}}{CH_3\text{-}Br} + \underset{\text{Reagent}}{\text{aq. NaOH}} \xrightarrow{298K} \underset{\text{Products}}{CH_3\text{-}OH} + \underset{\text{Products}}{NaBr}$$

This equation indicates conversion of bromomethane to methanol. In this organic reaction, the carbon-bromine bond (in bromomethane) is broken and a new bond between carbon and oxygen is formed giving methanol. *Thus, basically organic reactions involve breaking and making of covalent bonds.* **A sequential account of each step in terms of structure and energetics during bond breaking and bond formation that occurs when a reactant is transformed into the product is a subject referred to as *reaction mechanism*.** The knowledge of reaction mechanism helps in understanding the reactivity of organic compounds and in planning strategy for their synthesis.

The movement of electrons in organic reactions can be described by curved-arrow notation. It shows how changes in bonding occur due to electronic redistribution during the reaction. To show the change in position of a pair of electrons, curved arrow starts at an electron pair that participates in the reaction. If the electrons being shifted belong to a bond in the reactant then the curved arrow is drawn starting from the centre of the line representing the bond, and it ends pointing to the location of the new bond being formed in the product. If the electrons become a non-bonding pair in the product the arrow should point to the atom that accepts the non-bonding electrons, which may be shown by pair of dots. Movement of single electron is indicated with a single barbed 'fishhooks' (*i.e.*, half-headed curved arrow). For example, in the above reaction of bromomethane with hydroxide ion giving methanol, the movement of electrons using curved-arrows can be depicted as follows.



14.10.2 Fission of Covalent Bond

The cleavage of covalent bond can occur in two ways: (i) ***Heterolytic cleavage***, and (ii) ***Homolytic cleavage***.

In ***heterolytic cleavage***, the bond breaks in such a fashion that the shared pair of electrons remains with either of the previously joined atoms.

After heterolysis, one atom has a sextet electronic structure and a positive charge and the other will have a valence octet with at least one lone pair and a negative charge. Thus, heterolytic cleavage of bromomethane will give $^+CH_3$ and Br^- as shown above.

The species that has a sextet at the carbon and is positively charged is called a *carbocation* (earlier called *carbonium ion*). The $^+CH_3$ ion is known as a methyl cation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on the number of carbons that are directly attached to the positively charged carbon. Some examples of carbocations include $CH_3C^+H_2$ (ethyl cation, a primary carbocation), $(CH_3)_2C^+H$ (isopropyl cation, a secondary carbocation), and $(CH_3)_3C^+$ (*tert*-butyl cation, a tertiary carbocation). Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects, described earlier. The observed order of carbocation stability is: $^+CH_3 < CH_3C^+H_2 < (CH_3)_2C^+H < (CH_3)_3C^+$. These carbocations have trigonal planar shape with positively charged carbon being sp^2 hybridised. Thus, the shape of $^+CH_3$ may be considered as being derived from the overlap of three equivalent C(sp^2) hybridised orbital with hydrogen 1*s* orbital. Each bond may be represented as C(sp^2)-H1*s* sigma bond. The remaining carbon orbital is perpendicular to the molecular plane and

contains no electrons. (Fig. 14.4).

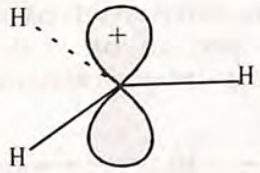
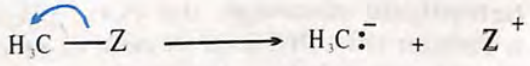


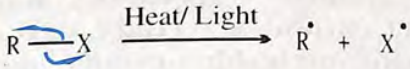
Fig. 14.4 Shape of methyl cation

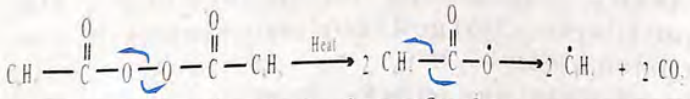
The heterolytic cleavage can also give carbon species, which contain the shared pair of electrons. For example, when group Z attached to the carbon leaves without electron pair, the



methyl anion $\left(H_3C:^-\right)$ is formed. Such a carbon species carrying a negative charge is called *carbanion*. Carbanions are also unstable and reactive species. The organic reactions which proceed through heterolytic bond cleavage are called **ionic** or **heteropolar** or just polar reactions.

In a ***homolytic cleavage*** one electron of a shared pair in the covalent bond goes with each of the bonded atoms. Thus, in homolytic cleavage, the movement of a single electron takes place instead of an electron pair. The single electron movement is shown by 'half-headed' curved-arrows. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called *free radicals*. Like carbocations and carbanions, free radicals are also very reactive. Some homolytic cleavages are shown in the following equations.





Alkyl radicals are classified as primary, secondary, or tertiary and their stability parallels to that of alkyl carbocations. Thus, alkyl radical stability increases as we proceed from methyl to tertiary:

$$\dot{C}H_3 < \dot{C}H_2CH_3 < \dot{C}H(CH_3)_2 < \dot{C}(CH_3)_3,$$

which can be explained on the basis of hyperconjugation. Organic reactions, which proceed by homolytic fission are called *free radical* or *homopolar* or *nonpolar* reactions.

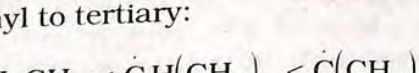
14.10.3 Nucleophiles and Electrophiles

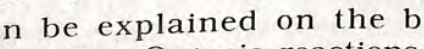
In polar reactions complementary pairs of reactive species are involved in covalent bond formation. These are an electron pair donor known as the *nucleophile* (Nu:) [nucleus seeking] and an electron pair acceptor known as the *electrophile* (E) [electron-seeking]. During a polar organic reaction, a nucleophile attacks an electrophilic centre, which is that specific atom or part of the electrophile that is electron deficient. Similarly, the electrophile bonds to a nucleophilic centre, which is the electron rich specific atom in part of the nucleophile. Thus, the electrophiles receive nucleophile's electron pair when the two undergo bonding interaction. A curved-arrow notation is used to show the movement of electrons from the nucleophile to the electrophile. Some examples of nucleophiles are the negatively charged ions with lone pair of electrons such as hydroxide (HO^-), cyanide (NC^-) ions and carbanions ($R_3C:^-$). Neutral molecules such as $H_2\ddot{O}:$, $R_3N:$, $R_2\ddot{O}:$ etc can also act as nucleophiles due to the presence of lone pair of electrons. Examples of electrophiles include carbocations and neutral molecules having functional groups like carbonyl group (>C=O) or alkyl halides (R_3C-X, where X is a halogen atom). The carbon atom in carbocations has sextet configuration and hence electron deficient and can receive a pair of electrons from the nucleophiles. In neutral molecules such as in alkyl halides, due to the polarity of the C-X bond a partial positive charge is generated on the carbon atom and hence the carbon atom becomes an electrophilic centre at which a nucleophile can attack.

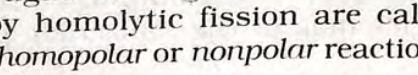
Example 14.19

Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds (shown in bold blue) undergo heterolytic cleavage.
(a) CH_3-SCH_3, (b) CH_3-CN, (c) CH_3-Cu

Solution

(a) 

(b) 

(c) 

Example 14.20

Giving justification, categorise the following molecules/ions as nucleophile or electrophile:

$HS^-, BF_3, C_2H_5O^-, (CH_3)_3N:,$

$\overset{+}{C}l, CH_3\overset{+}{C}=O, H_2N^-:, \overset{+}{N}O_2$

Solution

Nucleophiles: $HS^-, C_2H_5O^-, (CH_3)_3N:, H_2N^-:$

(Have unshared pair of electrons, which can be donated and shared with an electrophile).

Electrophiles: $BF_3, \overset{+}{C}l, CH_3\overset{+}{C}=O, \overset{+}{N}O_2$. Positive sites have only six valence electrons; can accept electron pair from a nucleophile.)

Example 14.21: Identify electrophilic centre in the following: $CH_3CH{=}O$, CH_3CN, CH_3I.

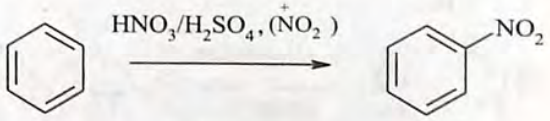
Solution

The starred carbon atoms are electrophilic centers as they will have partial positive charge due to polarity of the bond. $CH_3HC^*{=}O$, $H_3CC^*{\equiv}N$, $H_3C^*{-}I$

14.10.4 Classification of Organic Reactions

Organic reactions can be classified into the following common reaction types.

(i) Substitution reactions: Substitution reactions are those organic reactions in which one atom or a group of atoms in a molecule is substituted by another. The reaction of bromomethane with sodium hydroxide mentioned above in which bromine atom is replaced by hydroxide group is an example of a substitution reaction. In this reaction a nucleophile (HO^-) substitutes the Br atom in the substrate, hence it is termed as a *nucleophilic substitution reaction*. Similarly there are *electrophilic* and free *radical substitution* reactions also. Nitration of benzene giving nitrobenzene (*a*) is an example of an electrophilic substitution reaction in which $^+NO_2$ acts as an electrophile. The halogenation of alkanes (*e.g.* CH_4,) is an example of a free radical substitution reaction. The $Cl^{\cdot}$ free radical generated by the homolysis of Cl_2 initiates the reaction (See section 17.6.1).

(a) 

(b) $CH_4 + Cl_2 \xrightarrow{\text{Light}} CH_3Cl + HCl$

(ii) Addition reactions: Those organic reactions in which the reactants combine to form a single product having all the atoms of combining units are termed as addition reactions. For instance, the following reaction of but-1-ene with hydrogen bromide giving 2-bromobutane is an example of an addition reaction.

$$CH_3CH_2CH{=}CH_2 + HBr \longrightarrow CH_3\overset{Br}{C}H{-}\overset{H}{C}H_2$$

The addition reactions may be eletrophilic, nucleophilic or free radical types.

(iii) Elimination reactions: In an elimination reaction, two atoms or groups of the molecule are eliminated to give the product. Depending on the relative positions of the atoms or groups eliminated, these reactions are classified as α (alpha), β (beta), or γ (gamma) *elimination reactions* (See also section 17.6.2).

α-Elimination: In α-elimination, the two atoms of groups are removed from the position (α) giving electron deficient reactive intermediates, which further react to give stable product(s).

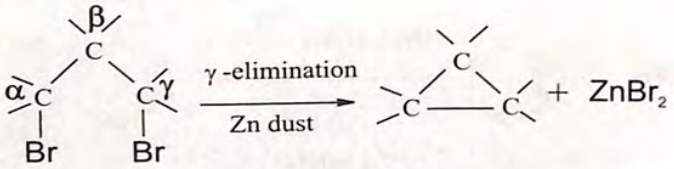
$$R_2\overset{H}{C}{-}Cl \xrightarrow{-H^+} R_2\ddot{C}{-}Cl \xrightarrow{-Cl^-} R_2C:$$

(carbene, reactive intermediate;)

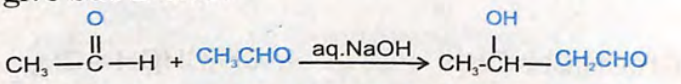
β-Elimination: In this, the two groups are removed from adjacent positions (α, β). Elimination of HBr from 1-bromobutane in presence of alcoholic potassium hydroxide giving but-1-ene is an example of such elimination.

$$CH_3\text{-}CH_2\overset{H}{C}H\text{-}CH_2Br \xrightarrow{KOH\ (alc.)} CH_3\text{-}CH_2CH{=}CH_2 + HBr$$

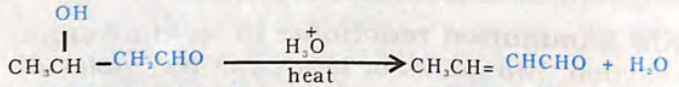
γ-Elimination: In such reactions the atoms or groups being removed are three bonds away, *i.e.* at *a* and γ positions. It involves formation of a three-membered ring as shown below.



(iv) Condensation reactions: In these reactions, two different or same organic reactants unite to give a product with or without elimination of another simple molecule. For example, two molecules of acetaldehyde condense in presence of alkali yielding 3-hydroxybutanal (aldol condensation), which loses a water molecule to give but-2-enal.

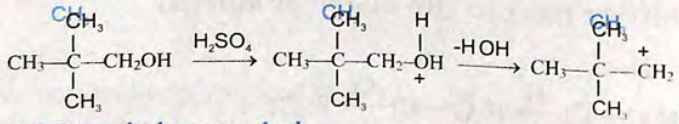


Ethanal (acetaldehyde) 3-Hydroxybutanal (aldol)

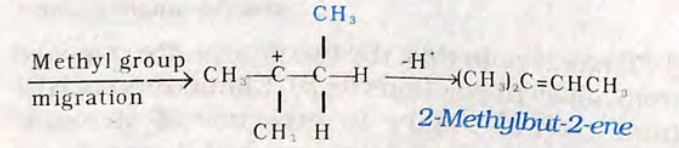


3-Hydroxybutanal But-2-enal

(v) Rearrangement reactions: These reactions involve migration of a group from one atom to another in the same molecule. For instance, under acidic condition, 1,2-migration of a $-CH_3$ group in 2,2-dimethylpropan-1-ol gives rearranged product 2-methylbut-2-ene.

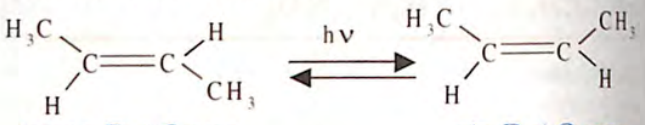


2,2-Dimethylpropan-1-ol



2-Methylbut-2-ene

(vi) Isomerisation reactions: These are reactions effecting interconversion of isomers wherein the molecular formulae and carbon skeletons of reactant and product always remain the same. The interconversion of *trans*-but-2-ene into *cis*-but-2-ene is referred to as geometrical isomerisation reaction.



trans-But-2-ene *cis-But-2-ene*

There are some other organice reactions, which do not involve ionic or free radical intermediates. These reactions occur in single step *via* a cyclic transition state. The bond breaking and making occurs simultaneously in these reactions. Such reactions are collectively called **pericyclic reactions.**

Example 14.22

Classify the following transformations according to the reaction type.

(a) $H_3C\text{-}CH{=}CH\text{-}CH_3 + Br_2 \rightarrow H_3C\text{-}CHBr\text{-}CHBr\text{-}CH_3$

(b) $(H_3C)_2C{=}C(CH_3)_2 + Br_2 \rightarrow (H_3C)_2C{=}C(CH_3)CH_2Br + HBr$

(c) $H_2C{=}CH\text{-}CH_2CH_3 \rightarrow H_3CCH = CHCH_3$

(d) $C_6H_5CHO + CH_3COCH_3 \rightarrow C_6H_5CH(OH)CH_2COCH_3$

(e) $(CH_3)_3CCl + HO^- \rightarrow (CH_3)_2C{=}CH_2 + H_2O + Cl^-$

(f) $CH_3C(Ph){=}N\text{-}OH + H_3O^+ \rightarrow CH_3\text{-}C(NHPh){=}O$

Solution

(a) Addition (b) Substitution (c) Isomerisation (d) Condensation (e) Elimination (f) Rearrangement.

SUMMARY

In this unit we have learned some basic concepts in structure and reactivity of organic compounds, which are formed due to **covalent bonding**. The nature of covalent bonding in organic compounds can be described in terms of **orbital hybridisation** concept, according to which carbon can have sp^3, sp^2, and sp hybridised orbitals. The sp^3, sp^2 and sp hybridized carbons are found in compounds like methane, ethene and ethyne respectively. The **tetrahedral shape** of methane, **planar shape** of ethene and **linear shape** of ethyne can be understood on the basis of this concept. A sp^3 hybrid orbital can overlap with $1s$ orbital of hydrogen to give a carbon-hydrogen (C-H) **single bond (sigma, σ bond)**. Overlap of a sp^2 orbital of one carbon with sp^2 orbital of another results in the formation of carbon-carbon σ bond. The unhybridised p orbitals on two adjacent carbons can undergo side-by-side overlap to give a **pi (π) bond**.

Organic compounds can be represented by various structural formulae including **complete**, **condensed** or **bond-line structural formula**. The 3-D representation of organic compounds can be made by **wedge and dash formula**. The 3-D arrangement of atoms in space for organic compounds can be represented in plane by different projection formulae such as **Fischer projection formula**, **Newman projection formula**, and **sawhorse projection formula**. The existence of two or more chemical compounds with the same molecular formula but having different properties owing to different arrangement of atoms within the molecule is termed as isomerism. There are two main types of isomerism: **constitutional** (also known as **structural isomerism**) and **stereoisomerism.**

Organic compounds are named by following a set of rules laid down by the International Union of Pure and Applied Chemistry (IUPAC). In **IUPAC nomenclature**, the names are correlated with the structure such that the reader or listener can deduce the structure from the name. Sometimes, organic compounds are also given **common** or **trivial names**. Organic compounds can be classified in families on the basis of **functional group** they contain. A functional group is an atom or group of atoms bonded together in a unique fashion and having characteristic chemical properties.

The concept of **resonance** is used to describe molecules that can not be adequately represented by one Lewis structure. Resonance involves electron delocalisation to represent the compounds by various Lewis structures. The actual molecule is understood to be a hybrid of all the possible **resonance structures**. No individual resonance structure is a true representation of the actual molecule. **Hyperconjugation** describes the orbital interactions between the π systems and the adjacent σ bonds of the substituent group(s) in organic compounds.

In **polar covalent bonds** bonding electrons are unequally shared and the electrons are drawn closer to the more electronegative atom of the bond. Polarisation of one σ bond caused by the polarisation of an adjacent σ bond is referred to as the **inductive effect**. The magnitude of inductive effect diminishes as the number of intervening σ bonds increases.

Organic reactions involve breaking and making of covalent bonds. A covalent bond can be cleaved in **heterolytic** or **homolytic** fashion. A **heterolytic cleavage** yields **carbocations** or **carbanions** while a **homolytic cleavage** gives **free radicals** as reactive intermediates. Reactions proceeding through heterolytic cleavages involve the complementary pairs of reactive species. These are an electron pair donor known as the **nucleophile** and an electron pair acceptor known as the **electrophile**. Organic reactions can be broadly categorised into the following **reaction types**: *substitution, addition, elimination, condensation, rearrangement and isomerisation.*

EXERCISES

14.1 Give hybridisation state of each carbon in following compounds: $CH_2=C=O$, $CH_3-CH=CH_2$, $(CH_3)_2CO$, $CH_2=CHCN$, $CH_3CH_2^{\cdot}$, $CH_3CH_2^{+}$, $CH_3CH_2^{-}$.

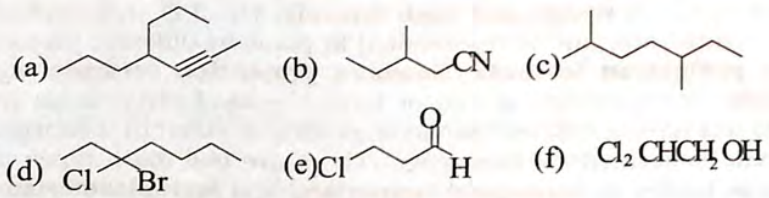
14.2 Indicate the σ and π bonds in the following molecules: C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2=C=CH_2$, CH_3NO_2, $HCONHCH_3$

14.3 Write bondline formulae for: *tert*-Butylcyclopentane, Isopropyl alcohol, 2,3-Dimethylbutanal, Heptan-4-one, Cyclohexanone.

14.4 Write stick, condensed and bondline structural formulae for all the possible isomers of molecular formula: C_4H_6, C_6H_{14}, C_6H_{10}, C_8H_{10}, C_8H_{18}, C_3H_8O, $C_3H_6O_2$, $C_4H_{10}O$, $C_6H_{11}NO_2$.

14.5 Draw structures of all isomeric ethers corresponding to molecular formula $C_5H_{12}O$.

14.6 Give the IUPAC names of the following compounds.

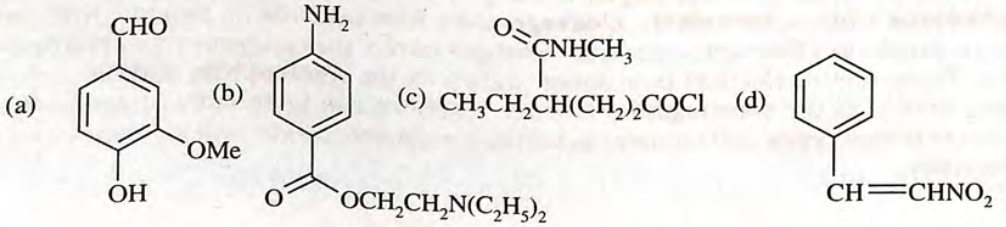


14.7 Which of the following represents the correct IUPAC name for the compounds concerned: (a) 2,2-Dimethylpentane or 2-Dimethylpentane, (b) 2,3-Dimethylpentane or 3,4-Dimethylpentane, (c) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane, (d) 2-Chloro-4-methylpentane or 4-Chloro-2-methylpentane, (e) But-3-yn-1-ol or But-4-ol-1-yne.

14.8 Draw formulae for the first five members of each homologous series beginning with the following compounds. (a) H-COOH, (b) CH_3COCH_3, (c) H-CH=CH_2

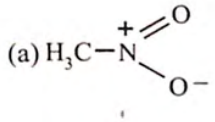
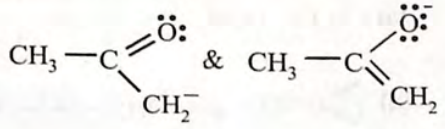
14.9 Give condensed and bondline structural formulae and identify the functional group(s) present, if any, for:
(a) 2,2,4-Trimethylpentane,
(b) 2-Hydroxy-1,2,3-propanetricarboxylic acid,
(c) Cycloocta-1,5-diene,
(d) Hexanedial,
(e) 2-(4-Isobutylphenyl)propanoic acid,
(f) 2-Hydroxy-1,2-diphenylethan-1-one.

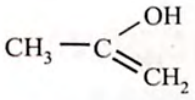
14.10 Identify the functional groups in the following compounds.



14.11 Draw the complete structures of bromomethane, bromoethane, 2-bromopropane and *tert*-butylbromide. Arrange them in order of increasing steric hindrance.

14.12 Which of the following pairs of structures do not constitute resonance structures?

(a)  & $H_3C-O-N=O$ (b) 

(c) $(CH_3)_2CO$ &  (d) $CH_3CH=CHCH_3$ & $CH_3CH_2CH=CH_2$

14.13 Which is expected to be more stable, $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ and why?

14.14 Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.

(a) C_6H_5OH, (b) $C_6H_5NO_2$, (c) $C_6H_5\overset{+}{C}H_2$, (d)$CH_3CH=CHCHO$, (e) $CH_3CH=CH-\overset{+}{C}H_2$, (f) C_6H_5CHO, (g) $CH_2=CHOCH_3$.

14.15 Explain why alkyl groups acts as electron donors when attached to a π system.

14.16 What are nucleophiles and electrophiles? Explain with examples.

14.17 Classify the reagents shown in bold in the following equations as nucleophiles or electrophiles. Use curved-arrow notation to show the electron movement.

(a) $CH_3COOH + \mathbf{HO^-} \rightarrow CH_3COO^- + H_2O$

(b) $CH_3COCH_3 + \mathbf{NC^-} \rightarrow CH_3C(CN)OHCH_3$

(c) $C_6H_6 + \mathbf{\overset{+}{C}H_3CO} \rightarrow C_6H_5COCH_3$

14.18 Classify the following reactions in one of the reaction type studied.

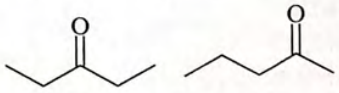
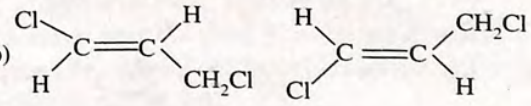
(a) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$

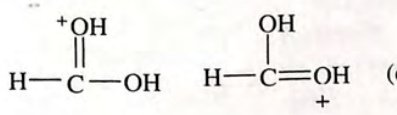
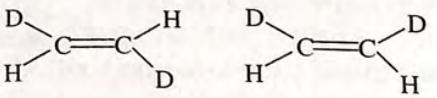
(b) $(CH_3)_2C=CH_2 + HCl \longrightarrow (CH_3)_2ClC-CH_3$

(c) $(CH_3)_3C-CH_2OH + HBr \longrightarrow (CH_3)_2CBr\ CH_2CH_3$

(d) $CH_3CH_2Br + HO^- \longrightarrow CH_2=CH_2$

14.19 What is the relationship between the members of following pairs of structures? Are they identical, structural or geometrical isomers, or resonance contributors?

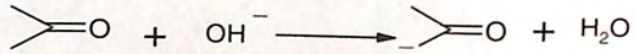
(a)  (b) 

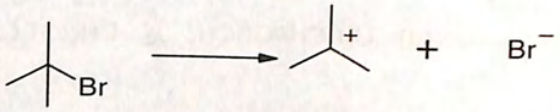
(c)  (d) 

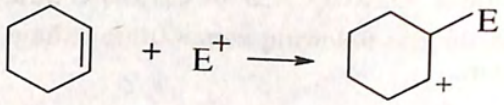
14.20 What are reactive intermediates? How are they generated by bond fission?

14.21 For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate products as free radical, carbocation and carbanion.

(a) $CH_3O - OCH_3 \rightarrow CH_3\dot{O} + \dot{O}CH_3$

(b) 

(c) 

(d) 

UNIT 15

HYDROCARBONS

Objectives

After studying this unit, you will be able to

- learn about nomenclature, preparation, physical and chemical properties of aliphatic and aromatic hydrocarbons.
- draw and describe conformations of simple alkanes like ethane, propane, butane and cycloalkanes like cyclohexane.
- explain geometrical isomerism in alkenes.
- know about petroleum, LPG and CNG and their uses.
- describe the structure of benzene and explain aromaticity and mechanism of electrophilic aromatic substitution and orientation.
- know about polynuclear hydrocarbons and their toxicity.

In this unit, we will discuss hydrocarbons, which are the compounds of carbon and hydrogen only. Hydrocarbons are obtained mainly from petroleum, natural gas and coal. Examples of hydrocarbons are methane, ethane, acetylene and benzene. The important fuels like petrol, kerosene, coal gas, oil gas, CNG(compressed natural gas), LPG(liquefied petroleum gas) etc. are all hydrocarbons or their mixtures.

The hydrocarbons are divided into two main categories – Aliphatic and Aromatic. The aliphatic hydrocarbons are further classified into saturated (alkanes), unsaturated (alkenes and alkynes) and alicyclic (cycloalkanes) hydrocarbons.

15.1 ALKANES AND CYCLOALKANES

They are also known as paraffins derived from the Latin words, 'parum' (little) and 'affinis' affinity, that is with little affinity. The name is justified as under normal conditions, alkanes are inert towards reagents like acids, bases, oxidising and reducing agents. However, under drastic conditions, i.e., at high temperature and pressure alkanes do undergo different types of reactions like halogenation, nitration, sulphonation, pyrolysis etc.

Alkanes have tetrahedral structure around carbon atom with average C-C and C–H bond lengths of 154 pm and 112 pm respectively (Unit 14).

Alkanes form a homologous series with the general formula, $C_n H_{2n+2}$, where n is the number of carbon atoms in the molecule. Methane, CH_4 with n = 1 and ethane, C_2H_6 with n = 2 are the first two members of the series.

Cycloalkanes are cyclic hydrocarbons which form a homologous series with the general formula $C_nH_{2n,}$, whose first member is cyclopropane(with n = 3).

15.1.1 Nomenclature

The nomenclature of alkanes has already been discussed earlier in Unit-14. A few more examples showing the application of rules of nomenclature are given below.

Example 15.1

Write IUPAC names for the following structures.

(i) $(H_3C)_4C$ (ii) $(H_3C)_2C(C_2H_5)\text{-}CH_2\text{-}C(CH_3)_3$

Solution

(i) 2,2-Dimethylpropane

(ii) 2,2,4,4-Tetramethylhexane

Example 15.2

Write the structure for the compounds having IUPAC names.

(i) 3-Ethyl-2-methylpentane

(ii) 3,4,8-Trimethyldecane

Solution

(i) $H_3C\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_3$

(ii) $H_3C\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}(CH_2)_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_3$

15.1.2 Preparation

Alkanes can be prepared as follows:

1. **From unsaturated hydrocarbons:** Hydrogenation of alkenes or alkynes in presence of catalysts like nickel, platinum or palladium gives alkanes,

$$RHC=CHR + H_2 \xrightarrow{\text{Catalyst}} RCH_2CH_2R$$

$$RC\equiv CR + 2H_2 \xrightarrow{\text{Catalyst}} RCH_2CH_2R$$

2. **From alkyl halides :** (i) Alkyl halides when reduced with zinc and hydrochloric acid or zinc copper couple and alcohol give alkanes,

$$RX + H_2 \rightarrow RH + HX$$

(ii) Alkyl halides when treated with sodium metal in dry ether solution give higher alkanes (Wurtz reaction),

$$RX + 2Na + XR \xrightarrow{\text{Ether}} R\text{-}R + 2NaX$$

If we take two different alkyl halides then we get a mixture of alkanes.

$$RX + 2Na + R'X \longrightarrow R\text{–}R + R'R' + RR'$$

3. **From carboxylic acids:** (i) On heating sodium salts of carboxylic acids with soda lime (mixture of calcium oxide and sodium hydroxide) alkanes are formed,

$$RCOO^-Na^+ \xrightarrow{CaO/NaOH} RH + Na_2CO_3$$

The process of elimination of carbon dioxide from a carboxylic acid is known as *decarboxylation.*

(ii) *Kolbe's Electrolytic method*: When an aqueous solution of sodium or potassium salt of a carboxylic acid is electrolyzed, a higher alkane is formed,

$$2RCOO^-K^+ + 2H_2O \xrightarrow{\text{Electrolysis}} R\text{-}R + 2CO_2 + H_2 + 2KOH$$

At anode the carboxylate ion ($RCOO^-$) gives up one electron to produce the free radical. $RCOO^\bullet$ which decomposes to give the alkyl radical and carbon dioxide.Two such alkyl radicals combine together to yield the higher alkane.

$$RCOO^- \xrightarrow{e^-} RCOO^\bullet \longrightarrow R^\bullet + CO_2$$

$$R^\bullet + R^\bullet \longrightarrow \underset{\text{Higher alkane}}{R\text{-}R}$$

Normally these two methods are useful for preparing alkanes containing even number of carbon atoms.

4. **Industrial source of alkanes**

Petroleum is the principal source for obtaining alkanes on large scale (For details See sub-section 15.1.5).

15.1.3 Properties

Physical Properties

The principal intermolecular interactions between alkane molecules are London dispersion interactions. Due to these weak forces the C_1 to C_4 alkanes are gases, C_5 to C_{17} liquids and those with more than 18 carbons are solids at 298 K. All of them are colourless and odourless. They are insoluble in water but for non-ionic compounds they themselves are good solvents.

The boiling point (b.p.) of alkanes increases steadily with increase in molecular mass. The increase is by 20^0 to 30^0 for each $-CH_2-$ unit added to the chain. (Table 15.1 shows the b.p./m.p. and molecular mass of some alkanes). Alkanes with straight carbon chains have higher boiling points than their isomers with branched

chains. Pentane, a straight chain hydrocarbon has most elongated molecular shape and has the highest boiling point of the three isomers. However, melting point depends also upon the packing of the molecules in the crystalline lattice. Therefore, neopentane, with a spherical molecular shape has the highest m.p. of the three isomers due to a more compact packing.

Pentane
(no branching)
b.p.309.1 K
m.p. 143.3 K

2-Methylbutane
(one branch)
b.p. 300.9 K
m.p. 113.1 K

2,2-Dimethylpropane
(Neopentane)
(two branches)
b.p. 282.5 K
m.p. 256.4 K

Chemical Properties

Alkanes are generally inert towards acids, bases, oxidising and reducing agents. However, they do undergo the following reactions:

1. Substitution reactions: The H-atom(s) of alkanes can be substituted by another atom or group by free radical mechanism (see Unit, 17) as exemplified below by the halogenation reaction.

Halogenation **:** The alkanes undergo substitution reaction with halogen (chlorine and bromine only) in presence of ultraviolet light or at high temperature (573 – 773 K) e.g.

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{Methylene chloride}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{Trichloromethane (Chloroform)}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{tetrachloromethane (Carbon tetrachloride)}}{CCl_4} + HCl$$

(See also unit 17)

2. Combustion: In presence of air or oxygen alkanes are completely oxidised to carbon dioxide and water and evolve large amount of heat. For example,

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l);\quad \Delta_c H^{\ominus} = -890\ kJmol^{-1}$$

The incomplete combustion of an alkane (e.g. methane) leads to the formation of carbon black used in manufacturing ink, printer ink, black pigments and as filters.

3. Oxidation: Alkanes can undergo oxidation under special conditions to yield a variety of products e.g.,

(i) $$2CH_4 + O_2 \xrightarrow[573K/1100\ atm]{Cu} \underset{\text{Methanol}}{2CH_3OH}$$

(ii) $$CH_4 + O_2 \xrightarrow{Mo_2O_3} \underset{\text{Formaldehyde}}{HCHO} + H_2O$$

Table 15.1 Variation of Melting Point and Boiling Point in Alkanes

Molecular Formula	Name	Molecular mass/u	b.p. K	m.p. K
CH_4	Methane	16	111.0	90.5
C_2H_6	Ethane	30	184.4	101.0
C_3H_8	Propane	44	230.9	85.3
C_4H_{10}	Butane	58	272.4	134.6
C_4H_{10}	2-Methylpropane	58	261.0	114.7
C_5H_{12}	Pentane	72	309.1	143.3
C_5H_{12}	2-Methylbutane	72	300.9	113.1
C_5H_{12}	2,2-Dimethylpropane	72	282.5	256.4
C_6H_{14}	Hexane	86	341.9	178.5
C_7H_{16}	Heptane	100	371.4	182.4
C_8H_{18}	Octane	114	398.7	216.2
C_9H_{20}	Nonane	128	423.8	222.0
$C_{10}H_{22}$	Decane	142	447.1	243.3
$C_{20}H_{42}$	Icosane	282	615.0	236.2

(iii) $2R\text{–}CH_3 + 3O_2 \xrightarrow{Ag_2O} 2RCOOH + 2H_2O$
Carboxylic acid

(iv) Alkanes having tertiary H can be oxidised to alcohols in presence of potassium permanganate.

$(CH_3)_3CH + O \longrightarrow (CH_3)_3C\text{–}OH$
tert- butanol

4. Isomerization: Alkanes isomerise to branched chain alkanes when heated with anhydrous aluminium chloride and hydrogen chloride.

$H_3C(CH_2)_4CH_3 \xrightarrow{\text{Anhyd. } AlCl_3/HCl}$
Hexane

$H_3C\underset{\underset{CH_3}{|}}{CH}CH_2CH_2CH_3 + H_3C CH_2 \underset{\underset{CH_3}{|}}{CH} CH_2 CH_3$
2-Methylpentane 3-Methylpentane

5. Aromatization: The alkanes containing 6 or more carbon atoms when heated at about 773 K under high pressure (10-20 atm), in presence of catalysts like oxides of chromium, vanadium or molybdenum supported on alumina get converted to aromatic hydrocarbons. This process is called *aromatization.*

$CH_3-(CH_2)_4-CH_3 \xrightarrow[773\text{ K, }10\text{–}20\text{ atm}]{Cr_2O_3 \text{ or } V_2O_5 \text{ or } Mo_2O_3} \text{C}_6\text{H}_6 + 4H_2$
Hexane Benzene

6. Reaction with steam: Methane reacts with steam at 1273 K in presence of nickel catalyst forming carbon monoxide and hydrogen.The method is used for industrial preparation of hydrogen.

$CH_4 + H_2O \xrightarrow{Ni} CO + 3H_2$

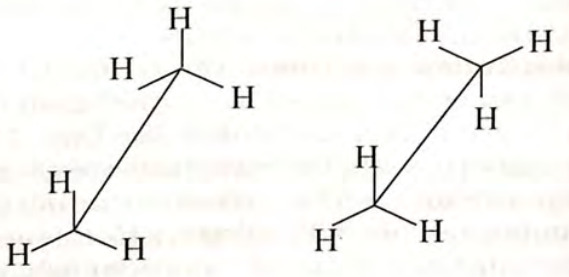
15.1.4 Conformations of Alkanes

Carbon atoms connected through σ bonds in alkanes can undergo rotation(Unit 14) leading to conformational isomers (conformers) or rotational isomers (rotamers). The rotation around a sigma bond is not completely free; it infact is hindered by an energy barrier of 1 to 20 kJ mol^{-1}. There is a possibility of weak repulsive interactions between the bonds or electron pairs of the bonds on adjacent carbon atoms. Such type of repulsive interaction is referred to as *torsional strain.*

Conformations of Ethane

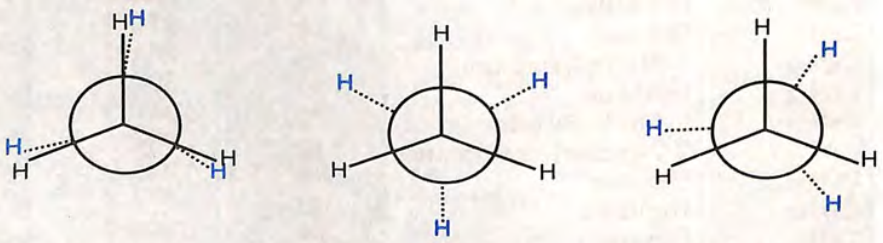
Ethane molecule contains a carbon – carbon single bond and each carbon is further attached to three H-atoms. If we allow one of the carbon atoms to rotate around the carbon – carbon bond keeping other carbon atoms stationary, infinite number of arrangemsents are possible.The two extreme conformations of ethane are (i) eclipsed form and (ii) staggered form, as shown below. All other possibilities in between are known as gauche or skew forms.

Conformations can be represented by sawhorse and Newman projections.



(i) Eclipsed (ii) Staggered

Fig.15.1 *Sawhorse projections of ethane*



(i) Eclipsed (ii) Staggered (iii) Skew

Fig.15.2 *Newman projections of ethane*

1. Sawhorse projection: In this projection the molecule is viewed along the axis of the model from above and right. The central C-C is drawn as a straight line slightly tilted to right for the sake of clarity.The line is drawn somewhat longer. The front carbon is shown as the lower left hand carbon whereas the rear carbon is shown as the upper right hand carbon. Each carbon has three lines corresponding to three atoms/groups (say H in case of ethane).

2. Newman projection: In this projection the molecule is viewed from the front. The carbon atom nearer to the eye is represented by a point and atoms (*e.g.* hydrogen) are shown as attached to it by three lines drawn at an angle of 120° to each other. The carbon farther from eye is represented by a circle and three atoms or groups (*e.g.* H in case of ethane) are shown to be attached to it by shorter lines at an angle of 120° to each other.

In eclipsed conformation of ethane the hydrogen atoms eclipse each other resulting in crowding, whereas in staggered conformation hydrogen atoms are as far apart as possible. The infinite number of possible intermediate conformations between eclipsed and staggered are called as skew conformations. The staggered conformation of ethane is more stable than eclipsed conformation. It is because in staggered form the H-atoms are far apart, therefore, the magnitude of repulsion is lesser than in eclipsed conformation. Hence, the order of stability follows the sequence: staggered > gauche (skew) > eclipsed. In accordance with the above discussion the Newman conformations of propane and butane are shown below:

Conformations of propane and butane:

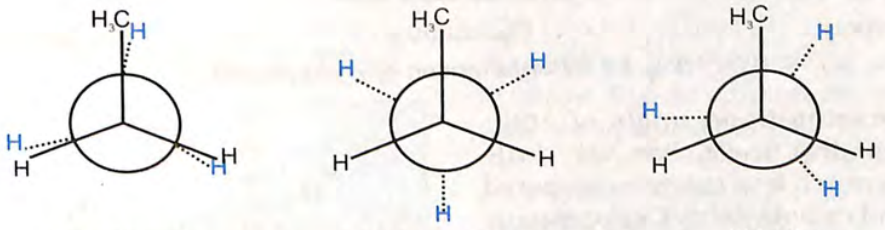
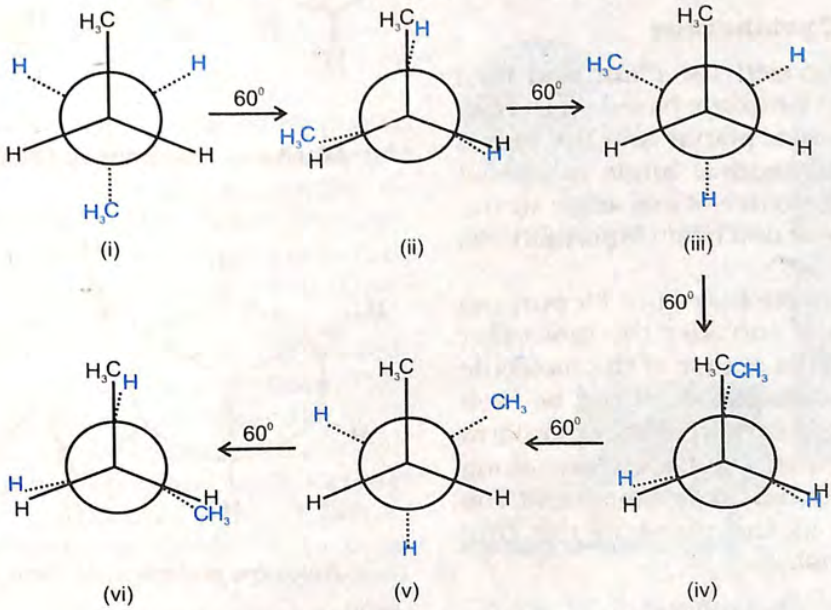


Fig.15.3 *Newman projections of propane*



(i) Anti; (ii), (iv) and (vi) Eclipsed ; (iii) and (v) Gauche

Fig.15.4 *Newman projections of butane (Changes with dihedral angle)*

Cycloalkanes

Like alkanes, cycloalkanes also show conformational isomerism. The bond angles in cyclopropane and cyclobutane are 60° and 90° respectively, (as shown below) compared to normal tetrahedral angle of 109.5° in saturated compounds (*e.g.* alkanes). The deviation of bond angles in cyclopropane and cyclobutane from normal tetrahedral angle introduces strain in the molecules of these cycloalkanes. In fact, greater the deviation, more strained is the molecule which leads to greater reactivity. Thus, cyclopropane with a bond angle of 60° is the most strained (of all cycloalkanes) and hence it is very reactive.

In chair conformation all C–H bonds are staggered (Newman projection), therefore it is most stable. While in boat conformation there is no angle strain but there is a significant torsional strain due to eclipsing of C-H bonds along C_2-C_3 and C_5-C_6 bonds (Newman projection).In addition to this ,the two hydrogens at C-1 and C-4 ,often called flagpole hydrogens ,interact with each other (non-bonded interaction) causing instability. Cyclohexane mainly exists in chair conformation and the boat form has only a transient existence. The chair form is stabler than the boat conformation, by about 44 kJ mol^{-1}.

Cyclopropane *Cyclobutane* *Cyclopentane*

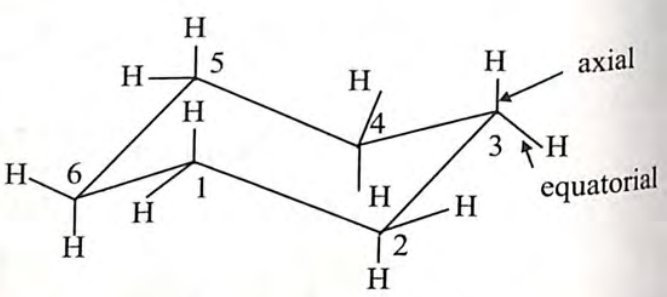
Fig.15.5 *Conformation of cycloalkanes*

Cyclopentane having bond angle of 108°, close to the tetrahedral angle, has very little strain and hence is much less reactive compared to cyclopropane and cyclobutane. Cyclopropane is planar, cyclobutane is almost planar while cyclopentane and cyclohexane are non-planar.

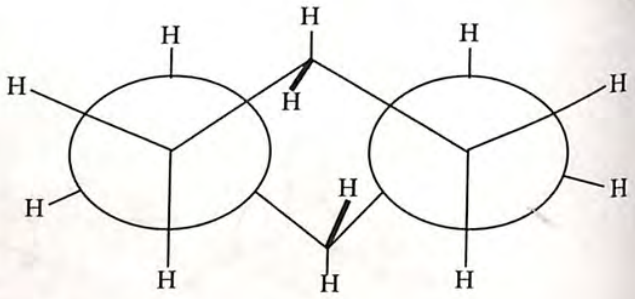
Conformations of Cyclohexane

Herman Sachse proposed the chair and boat conformations for cyclohexane based on the fact that the molecule is non planar and the ring is puckered. Thus, tetrahedral angle is almost retained and molecule is free of any angle strain. The two forms, *i.e.* chair and boat conformations, are shown in Fig.15.6.

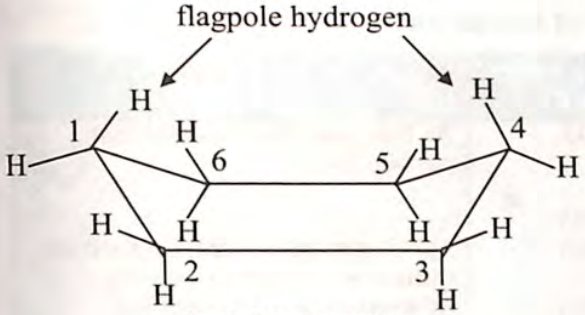
Although the ring is puckered but for purpose of discussion, we may consider the molecular axis to pass through the centre of the molecule and perpendicular to its plane. It can be seen from Fig.15.6 that each carbon in the chair form of cyclohexane has two C – H bonds, one along the molecular axis (axial hydrogens) and the other more or less in the plane of the ring (equatorial hydrogens).



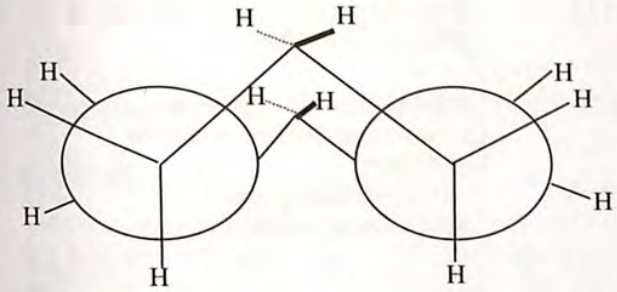
Sawhorse Projection of Chair Conformation



Newman projection of chair conformation



Boat Conformation



Newman projections of boat conformation

Fig.15.6 *Conformations of cyclohexane*

Example 15.3

How many eclipsed conformations are possible in butane ?

Solution

Three conformations

15.1.5 Petroleum

Petroleum (from Latin: *petra* meaning rock and *oleum* meaning oil) is a dark viscous oily liquid and is considered to be of biological origin. It is believed to be formed by the decomposition of marine animals under high pressure and temperature. The chief oil producing countries of the world are Saudi Arabia, Iran, Iraq, Russia, United States of America (USA), United Kingdom (UK), Mexico, China and India. The main oil producing centres in India are located in Gujarat, Assam and Mumbai. Petroleum occurs underground deep below earth's crust trapped within rock structure or much below the sea bed. Petroleum or crude oil as it is obtained is a complex mixture of hydrocarbons (chiefly aliphatic with lesser amounts of aromatic hydrocarbons) along with small amounts of organic compounds of sulphur and nitrogen. It is obtained by drilling holes in the earth's crust. Due to the pressure exerted by the natural gas, the oil rushes out through the pipes. After the pressure of the gas diminishes, two coaxial pipes are lowered into the bore and compressed air is forced through the pipe. This results in the oil coming out through the oil pipe. From the oil fields, the crude oil is taken to the refineries through pipelines.

Refining of Petroleum

The process of separating petroleum into different fractions having different boiling ranges is called **refining**. First, the oil is washed with acidic or basic solution depending upon whether the impurities are basic or acidic in nature. The washed oil is then subjected to fractional distillation by heating it to about 723 K and allowing the vapours to pass through a fractionating column. By this process the crude oil is separated into a number of fractions (Fig.15.7). The important petroleum fractions along with their approximate composition, boiling range and uses are given in Table 15.2.

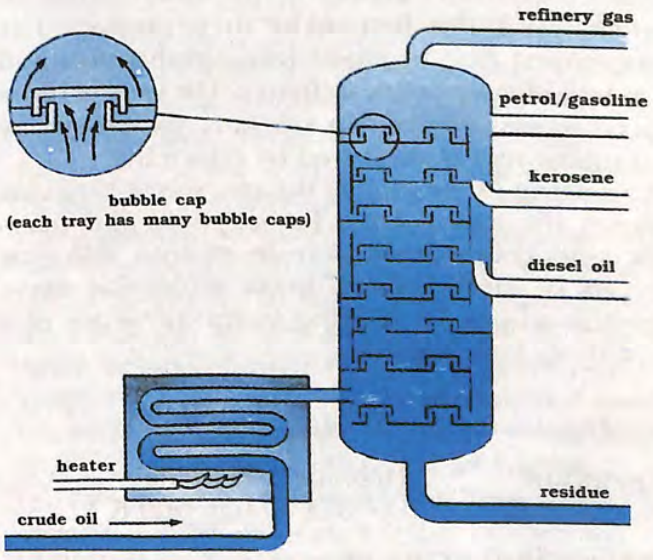


Fig.15.7 *Fractional distillation of crude oil*

Table 15.2 Fractions of Petroleum

S.No	Fraction	Approximate composition	Boiling range (in K)	Uses
1	Gaseous hydrocarbons	C_1 - C_4	Upto 303	As fuel gas after liquefaction, carbon black
2	Crude naphtha	C_5 - C_{10}	303 - 423	
	i) Petroleum ether	C_5 - C_7	303 - 363	As solvent in varnish and rubber industries, for dry cleaning
	ii) Petrol or gasoline	C_7 - C_9	363 - 393	As motor fuel, dry cleaning
	iii) Benzine	C_9 - C_{10}	393 - 423	For dry cleaning
3	Kerosene oil	C_{10} - C_{13}	423 - 513	Fuel for stoves, manufacture of oil gas, illuminant
4	Fuel oil i) Gas oil ii) Diesel oil iii) Furnace oil	C_{13} - C_{18}	513 - 623	Fuel for diesel engine and tractors, cracking stock for gasoline
5	Lubricant oil i) Medicinal oil ii) Motor oil iii) Grease	C_{15} - C_{18}	Above 543	Paint oil, transformer oil, lubrication, sizing paper
6	Paraffin wax i) Petroleum jelly ii) Petroleum wax iii) Petroleum coke	C_{18}-C_{30}	673 upward	Ointments, candles, paraffin wax, for matches, paints, water proofing, solid fuel, protecting paints
7	Heavy fuel oil and Bitumen	C_{30} onwards	Forms residue	Paints, road surfacing

Cracking and Reforming

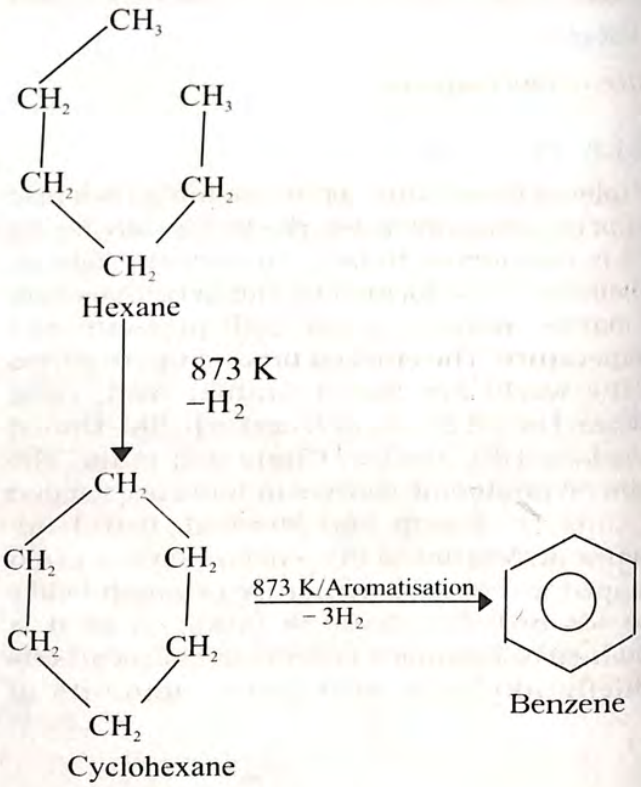
Gasoline (petrol), kerosene and diesel oil are the most important fractions of fractional distillation of crude oil. The demand for these products has increased due to rapid industrialisation and growth of automobile industry. The yield of these products is increased by cracking and the quality of motor fuel is improved by reforming.

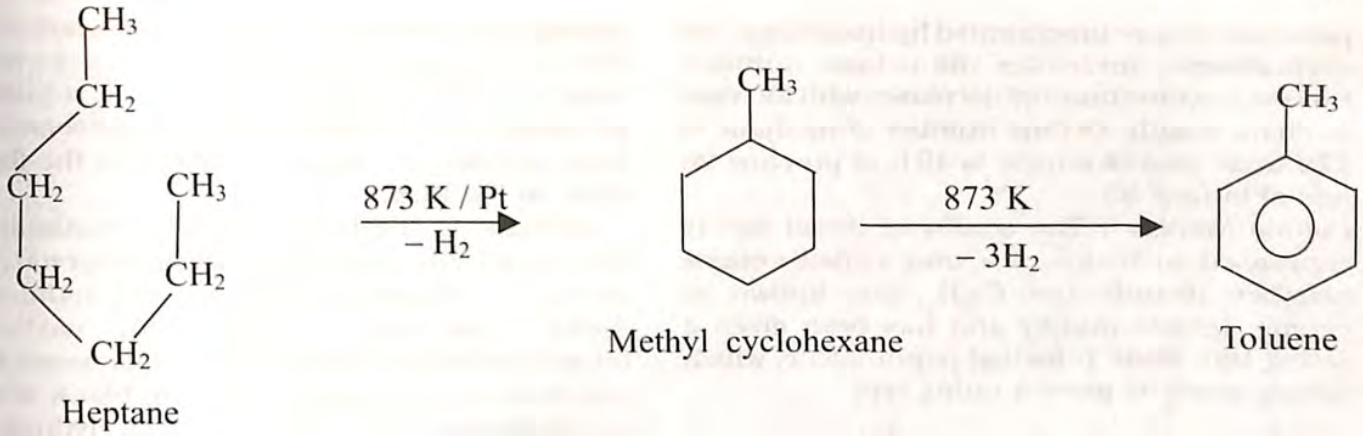
Cracking **:** Cracking is the process of breaking down the less volatile higher molecular mass hydrocarbons from petroleum into different types of more volatile lower molecular mass hydrocarbons by heating in the presence of a catalyst. For example,

$$C_{12}H_{26} \xrightarrow{973\ K/catalyst} C_7H_{16} + C_5H_{10}$$

Dodecane b.p. 489 K — Heptane b.p. 371 K — Pentene b.p. 309 K

Reforming **:** In this process alkanes containing 6-8 carbon atoms are heated at about 873 K in presence of a catalyst (platinum, palladium or nickel) leading first to cyclization and then to aromatisation or dehydrogenation.





Heptane Methyl cyclohexane Toluene

This process is used for the manufacture of aromatic hydrocarbons, such as benzene, toluene etc. from alkanes.

Synthetic Petrol or gasoline

In view of the depleting crude oil reserves, synthetic methods have been developed for the manufacture of petrol. These are:

(i) ***Fisher-Tropsch process*** : In this process, water gas (a mixture of CO and H_2) produced by passing steam over heated coal is mixed with excess hydrogen and heated to 473-523 K at 1-10 bar in the presence of Co or Ni. Under these conditions, a mixture of hydrocarbons is obtained which is fractionally distilled, as described earlier.

(ii) ***Bergius process*** : In this process, finely powdered coal is made into a paste with heavy oil. The paste is then heated in the presence of hydrogen at 773-873 K at 200-250 bar using iron oxide as catalyst.

The product is fractionally distilled to get desired products. These processes are useful particularly in countries which are rich in coal but poor in oil reserves.

Knocking : A sharp metallic rattling sound produced in an internal combustion engine is known as **knocking**. This causes loss of energy. The tendency of knocking decreases in the order, straight chain alkane > branched chain alkane > alkenes > cycloalkanes > aromatic hydrocarbons

Knocking can be reduced by adding antiknock compounds to petroleum *e.g.* tetraethyl lead $(C_2H_5)_4Pb$ which is a source of the free radical ($^{\bullet}C_2H_5$). The free radicals convert the straight chain alkanes to brached chain alkanes.

Due to toxic effects of lead and other environmental problems, the use of tetraethyl lead has been prohibited. The quality of petrol (gasoline) including its knocking behaviour is improved by other methods like aromatisation and isomerisation or by adding *iso* compounds.

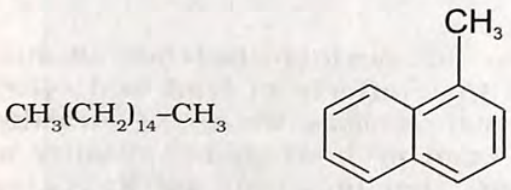
Quality of Petrol

Octane Number **:** Octane number is a scale which is used to determine the knocking quality of a fuel in an internal combustion engine. The two pure hydrocarbons heptane and isooctane have been selected as standards.

Heptane (CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3) is a straight chain hydrocarbon having very high knocking property when used as fuel, has been arbitrarily assigned an octane number zero. Isooctane i.e. 2,2,4-trimethylpentane (CH_3-$C(CH_3)_2$-CH_2-$CH(CH_3)$-CH_3) incorrectly known as iso-octane, a branched chain hydrocarbon having lowest knocking property, is given an octane number 100. The octane number is defined as the percentage of isooctane present in a mixture of isooctane and heptane, when the mixture has the same knocking performance in the experimental engine as the gasoline under examination.All fuels are graded on the basis of their octane number ranging from zero to 100. Higher the octane number, better is the quality of fuel. Gasoline used in automobiles should have an octane number 80 or higher, while gasoline used in aeroplanes has an octane number 100 or even higher. Recently, the hydrocarbons 2,2,3-trimethylpentane (CH_3-$C(CH_3)_2$-$CH(CH_3)$-CH_2-CH_3) called triptane has been assigned an octane number, 125. It is reported that branching of a hydrocarbon chain,

presence of more unsaturated hydrocarbons and cycloalkanes increases the octane number. However, octane number decreases with increase in chain length. Octane number of methane is 122 while that of ethane is 101, of propane 96 and of butane 89.

Cetane Number : The quality of diesel fuel is expressed in terms of a unit called **cetane** number. Hexadecane, $C_{16}H_{34}$ also known as cetane, ignites rapidly and has been given a rating 100, while 1- methyl naphthalene, which ignites slowly is given a rating zero.



$CH_3(CH_2)_{14}–CH_3$ Cetane

1-Methylnaphthalene

The ***cetane number*** is defined as percentage of cetane by volume in a mixture of cetane and 1- Methylnaphthalene, which has same ignition quality as the sample fuel under examination.

Petrochemicals and their Applications

The numerous organic chemicals derived from petroleum sources are termed "Petrochemicals". Petroleum is the most important source of a very large number of organic compounds required for industries. The major hydrocarbons obtained from petroleum refinery are given in the flow chart in Fig.15.8.

Methane is the major source of methanol, formaldehyde, formic acid, halogenated methanes which include methyl halides, dichloromethane, chloroform, carbon tetrachloride and mixed halides like freons in addition to acetylene, carbon black and synthesis gas or water gas ($CO + H_2$). Hydrogen from synthesis gas is used for hydrogenation and nitrogen fixation. Ethylene oxide prepared from ethene can be converted into a large number of organic chemicals. Acetone, acetic acid, acetaldehyde, glycols are generally obtained from ethylene or propene/butene and acetylene. A large number of monomers required for making polymers, rubbers, synthetic fibers are also obtained from these hydrocarbons. These monomers include vinyl halides, vinyl acetate, butadiene, isoprene, adipic acid, phthalic acid, styrene and hexamethylenediamine etc.

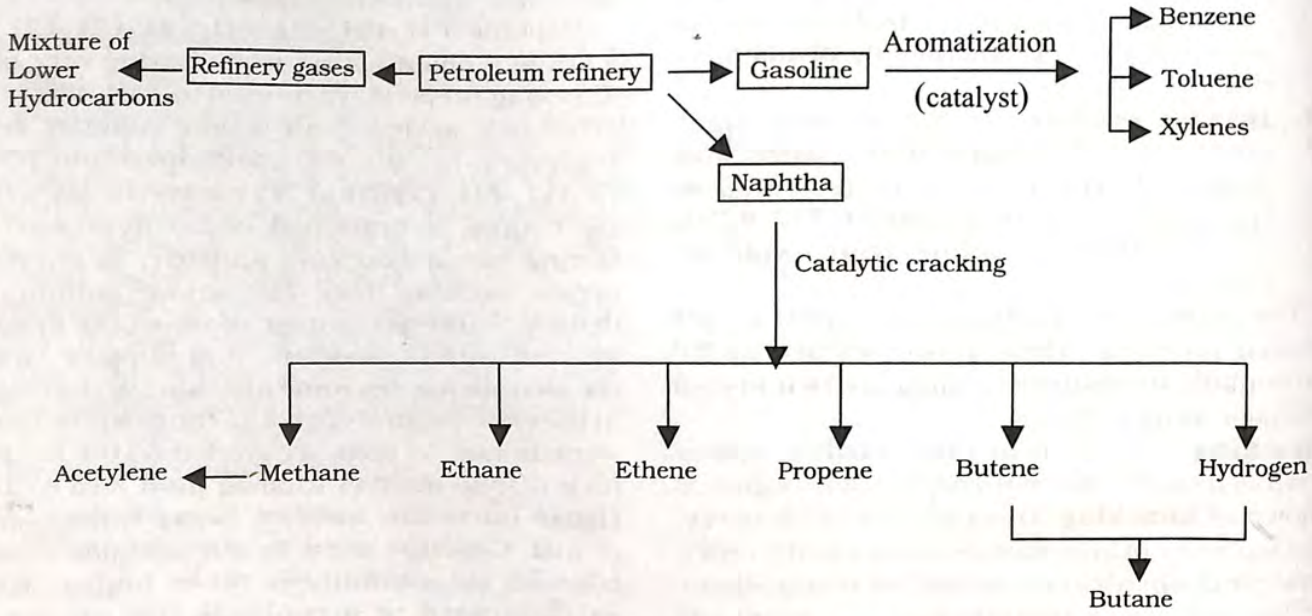
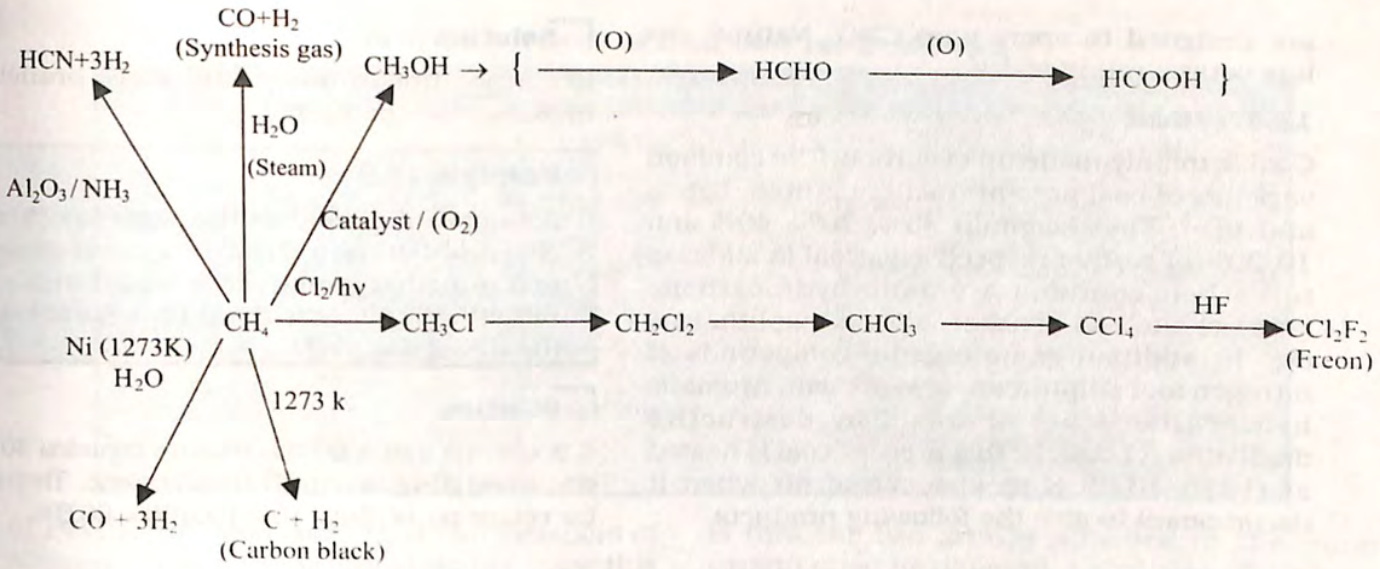
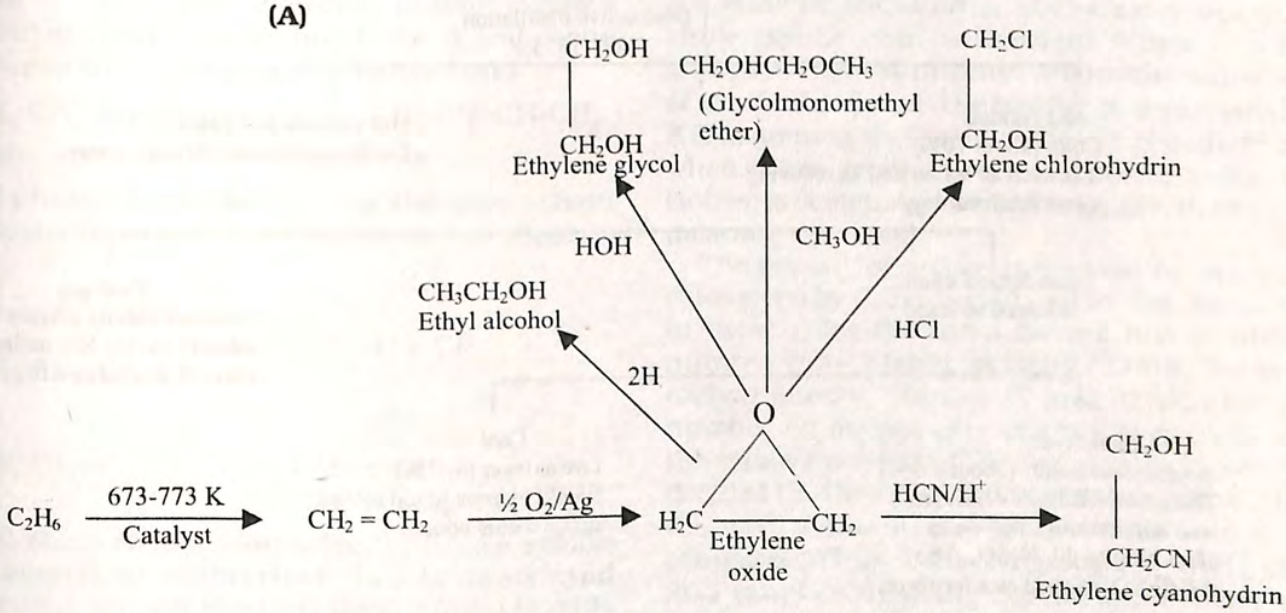


Fig.15.8 Hydrocarbons from petroleum refinery



(A)



(B)

Industrial preparation of some important chemicals from (A) methane and (B) ethane

15.1.6 LPG and CNG

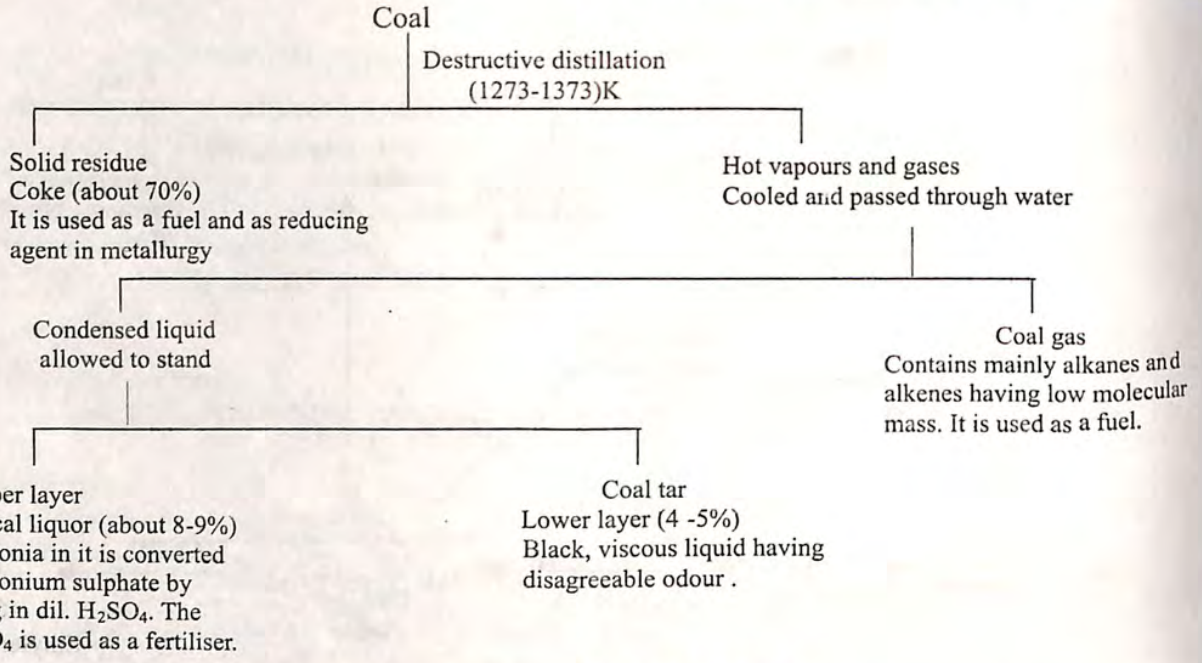
The term LPG (liquified petroleum gas) refers to mixtures of hydrocarbons containing three or four carbon atoms. This includes propane (C_3H_8), propene (C_3H_6), n-butane (C_4H_{10}), isobutane (methylpropane) and various butenes with small amount of ethane (C_2H_6). The major sources of LPG are natural gas and from refining and cracking of petroleum. Alkenes are mainly produced during cracking. LPG is mainly used for manufacture of chemicals, as a fuel for households and petrochemical industry.

CNG (Compressed Natural Gas) is highly compressed form of natural gas. Many vehicles

are designed to operate on CNG. Natural gas has octane rating of 130.

15.1.7 Coal

Coal is mainly made up of carbon. The common varieties of coal are anthracite, bitumin, lignite and peat. These contain 95%, 70%, 40% and 10-20% of carbon respectively. Coal in addition to carbon contains aromatic hydrocarbons (arenes) such as benzene, xylene, naphthalene etc. In addition some organic compounds of nitrogen and sulphur are also present. Aromatic hydrocarbons are obtained by destructive distillation of coal. In this process coal is heated at (1273–1373) K in absence of air when it decomposes to give the following products.


Coal
Destructive distillation
(1273-1373)K
Solid residue
Coke (about 70%)
It is used as a fuel and as reducing agent in metallurgy
Hot vapours and gases
Cooled and passed through water
Condensed liquid
allowed to stand
Coal gas
Contains mainly alkanes and alkenes having low molecular mass. It is used as a fuel.
Upper layer
Ammonical liquor (about 8-9%)
The ammonia in it is converted into ammonium sulphate by absorbing in dil. H_2SO_4. The $(NH_4)_2SO_4$ is used as a fertiliser.
Coal tar
Lower layer (4 -5%)
Black, viscous liquid having disagreeable odour .

Coal tar was earlier considered to be a nuisance. Even its disposal was a problem. Subsequently it was used for surfacing roads. It has now been found to be a rich source of aromatic hydrocarbons. Coal tar is subjected to fractional distillation and the fractions obtained are given in Table 15.3.

Example 15.4

Which of the following compounds has highest octane rating and why?

(i) $H_3C\text{-}(CH_2)_4\ CH_3$

(ii) $H_2C{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

(iii) $(H_3C)_2\text{-}\ C{=}CH\text{-}CH_2\text{-}CH_3$

(iv) $(H_3C)_2C{=}CH\text{-}CH\ (CH_3)_2$

Solution

(iv), since unsaturation and more branching increases octane rating.

Example 15.5

A sample of diesel has the same knocking characteristic as a 60 mL mixture of cetane and α-methyl naphthalene mixed in 2 : 1 ratio (V/V). What is the cetane number of the diesel sample?

Solution

It is obvious that a 60 mL mixture contains 40 mL cetane and 20 mL of α-methyl naphthalene. Therefore, the cetane no. of diesel $40 \times 100/60 = 66.6\%$.

15.2 ALKENES

The unsaturated hydrocarbons containing C=C bond and having general formula C_nH_{2n} are called alkenes. The simplest member of the alkene family is ethene, C_2H_4, which contains 5 σ bonds and 1 π bond. The carbon – carbon double bond is made up of a σ bond and a π bond. The bond enthalpy of C=C is 610 kJ mol^{-1} while carbon – carbon bond enthalpy of ethane is (370 kJ mol^{-1}). As a result of this C–C bond length in ethene (134 pm) is shorter than the C–C bond length in ethane (154 pm).

15.2.1 Isomerism in Alkenes

Alkenes generally show the types of isomerism given here :

Table 15.3 Fractions from Coal Tar Distillation

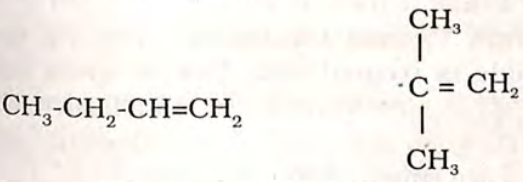
Fraction Name	Temperature range (k)	Major components
1. Light oil	Up to 443	Benzene, toluene, xylenes etc.
2. Middle oil or Carbolic oil	443 – 503	Phenol, naphthalene, pyridine
3. Heavy oil or Creosote oil	503 – 543	Methyl and higher alkyl phenols, naphthalene, napthols etc.
4. Green oil or Anthracene oil	543 – 633	Anthracene, phenanthrene
5. Pitch (residue)	Non – volatile	Used for making black paints, varnish for wood for water proofing and construction of roads

(i) *Position Isomerism* : First two members of alkenes (ethene and propene) do not show this type of isomerism. However, butene exhibits position isomerism as but-1-ene & but-2-ene differ in the position of the double bond.

CH_3-CH_2-CH=CH_2 CH_3-CH=CH-CH_3

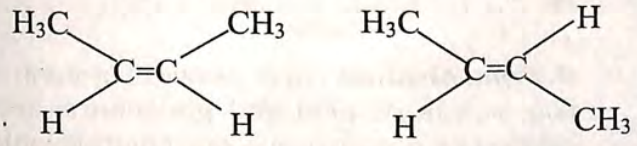
But-1-ene But-2-ene

(ii) *Chain Isomerism* : Butene also shows chain isomersim as isobutene has branched chain.



But-1-ene Isobutene
(2-Methylpropene-1)

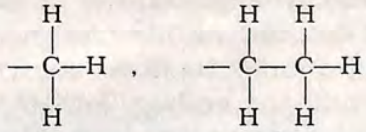
(iii) *Geometrical isomerism* : Alkenes exhibit geometrical isomerism due to restricted rotation around the C=C bond (Unit 14). This results in two possible arrangements of groups attached to the two doubly bonded carbon atoms, as shown below for but-2-ene,



cis-But-2-ene (Z) *trans*-But-2-ene *(E)*

This isomerism is also called as *cis-trans* isomerism .When the groups of similar nature are on the same side of the double bond, the isomer is designated as *cis* and when they are on opposite sides, as *trans*. The necessary and sufficient condition for geometrical isomerism is that the two groups attached to the same carbon must be different, i.e. olefins of the type abC=Cab or abC=Ccd or abC=Cax or abC=Cbx show *geometrical* isomerism.When the two groups of highest priority are on the same side of the double bond ,the isomer is designated as *Z* (Zusammen in German means together) and when these groups are on opposite sides, the isomer is designated as *E* (Entegegen in German meaning opposite).

The priority of groups is decided by sequence rules given by Cahn-Ingold and Prelog. According to these rules the atom having higher atomic number gets higher priority. Thus, between carbon (atomic number 6) and oxygen (atomic number 8), oxygen gets priority over carbon. If the relative priority of the two groups cannot be decided i.e. their **bonded atoms are same**, then the next atoms in the groups (and so on) are compared. Thus, between groups methyl (-CH_3) and ethyl (-CH_2CH_3), the latter will get the priority since the next atoms in methyl is H while in ethyl it is C (carbon has higher atomic number than hydrogen), as shown below



Example 15.6

Which of the following compounds will show cis-trans isomerism?

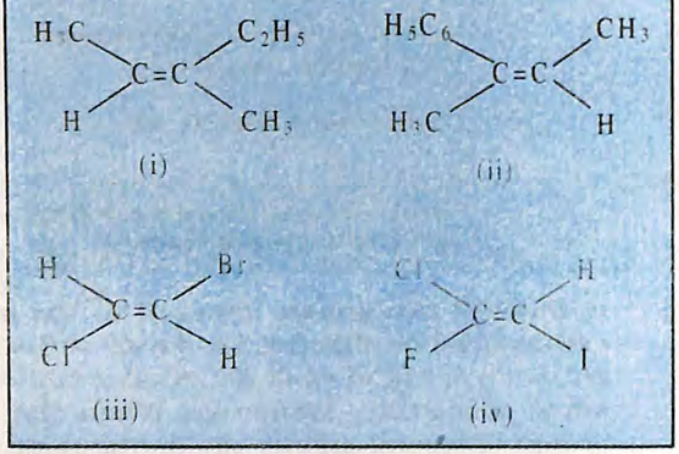
(i) $(H_3C)_2C$=CH-CH_3
(ii) H_2C=CCl_2
(iii) C_6H_5(H)C=CH-CH_3
(iv) H_3C-CH=CBr(CH_3)

Solution

(iii) and (iv)

Example 15.7

Classify the following as *Z* or *E* isomers.



Solution

(i) *Z* (ii) *Z* (iii) *E* (iv) *E*

15.2.2 Nomenclature

Two systems are prevalent for naming alkenes.

1. The Common System : The common names of first few alkenes are derived from corresponding alkanes by replacement of 'ane' by 'ylene', *e.g.* $H_2C = CH_2$ is ethylene.

2. IUPAC System : In this most commonly used system the ending 'ane' of corresponding alkanes is replaced by 'ene' The parent chain, is considered to be one corresponding to the longest chain of carbon atoms containing the double bond. The next longest chain may be selected provided it contains the maximum number of double bonds present. It is then numbered, starting from the end nearest to the double bond. The position of double bond is indicated by the number of carbon atom preceding the double bond. If there are 2 or more double bonds the ending 'ane' of alkanes is replaced by 'adiene or atriene'etc. The remaining rules are the same as applicable to alkanes.(see Unit 14). Some examples are given below,

$H_2C = CH_2$	Ethene
$H_3C - CH = CH_2$	Propene
$H_3C - CH_2 - CH = CH_2$	But-1-ene
$H_3C - CH = CH - CH_3$	But-2-ene
$(H_3C)_2C = CH_2$	2 –Methy-propene
$H_2C = CH - CH_2 = CH_2$	Buta-1, 3-diene
$H_2C = CH - \underset{\displaystyle CH = CH_2}{\underset{\vert}{CH}} - CH_2 - CH_2\,CH_3$	3-Propyl-penta-1, 4-diene

The locant for double bond may be written preceding or following the name of the parent alkane or following the root name followed by the suffix ene or diene or triene. All the three names i.e,1,3-butadiene, butadiene-1,3 or buta-1,3-diene are correct for butadiene.

15.2.3 Preparation

1. From Alkyl halides: Alkenes can be obtained by dehydro-halogenation of alkyl halides in presence of alcoholic potash.

$$RH_2C - CH_2 - X \xrightarrow{\text{Alc. KOH}, \Delta} RHC = CH_2 + HX$$

(X = Cl, Br, I)

This is an elimination reaction. The ease of dehydrohalogenation for different halogens is iodine > bromine > chlorine, while for carbons it is tertiary > secondary > primary i.e. a tertiary alkyl iodide is most reactive.

2. From Vicinal Dihalides : When a vicinal dihalide is treated with zinc, it gives alkene through elimination reaction. Dihalides in which the halogens are present on adjacent carbon atoms are called vicinal dihalides.

$$CH_2Br - CH_2Br + Zn \longrightarrow CH_2 = CH_2 + ZnBr_2$$

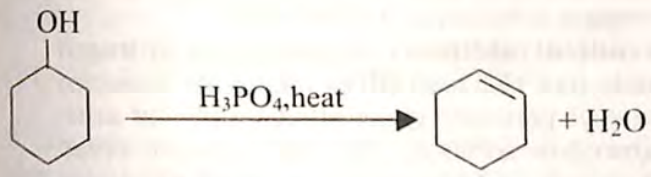
3. From Alkynes : Alkynes can be reduced to alkenes by reduction, i.e. using palladium-charcoal catalyst in catalytic hydrogenation or sodium in liquid ammonia as a reducing agent.

$$R - C \equiv C - R \xrightarrow[Na/Liq.NH_3]{Pd/C, H_2 \text{ or}} RHC = CHR$$

4. From Alcohols : In presence of protonic acids (*e.g.* sulphuric acid and phosphoric acid) or catalysts *e.g.* anhydrous zinc chloride, alumina etc. the alcohols can be dehydrated (removal of water) to alkenes.

$$C_2H_5OH \xrightarrow{H^+, \text{ heat}} H_2C = CH_2 + H_2O$$

$$RCH_2CH_2OH \xrightarrow{Al_2O_3, \text{ heat}} RHC = CH_2 + H_2O$$



This is an elimination reaction i.e. a molecule of water is eliminated.

15.2.4 Properties

Physical properties : Alkenes as a class have physical properties similar to those of alkanes.

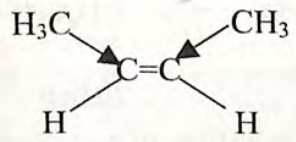
(i) First three members are gases, next fourteen members are liquids and higher ones are solids.

(ii) They are lighter than water and insoluble in water but soluble in organic solvents like benzene, ether etc.

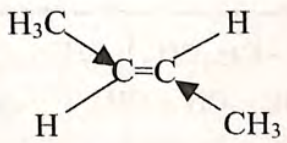
(iii) Their boiling points (b.p.) increase with increase in the number of carbon atoms, for each added $-CH_2$ group b.p. rises by 20^0 to 30^0. Their b.ps. are comparable to alkanes with corresponding carbon skeleton.

(iv) Alkenes are weakly polar. The π electrons of the double bond can easily be polarized. Therefore, their dipole moments are higher than those of alkanes.

(v) The dipole moment, melting points and boiling points of alkenes are dependent on the position of groups bonded to the two doubly bonded carbons. Thus,



cis-But-2-ene (small dipole moment)
b.p. 277 K, m.p. 134 K



trans-But-2-ene (no dipole moment)
b.p. 274 K, m.p. 167 K

cis -but-2-ene with two-methyl groups on the same side has a small resultant dipole while in *trans*-but-2-ene the bond moments cancel out. Due to relatively high polarity of the *cis*- isomer compared to its *trans* isomer, the former has higher b.p. Due to higher symmetry of the *trans* isomer it fits well into crystalline lattice and, therefore, generally has higher m.p. than the *cis* isomer. However, this is not a general rule and there may be exceptions. The measurement of dipole moment is a method to assign configuration to geometrical isomers.

Chemical properties: The most important reactions of alkenes are electrophilic additions and free radical additions. We have already studied such reactions in Unit 14.

A. Electrophilic addition

1. Addition of hydrogen halides : Hydrogen halides (HCl, HBr, HI) readily add to alkenes forming alkyl halides. The order of reactivity of hydrogen halides in this reaction is HI>HBr> HCl.

$$H_2C = CH_2 + HX \rightarrow H_3C - CH_2X \quad (X= I, Br, Cl)$$

It is an electrophilic addition reaction and proceeds through the formation of carbocations. Addition of acids HX takes place in two steps,

$$\text{(i)}\ H_2C = CH_2 + H^+ \xrightarrow{\text{slow}} H_2C^+ - CH_3$$

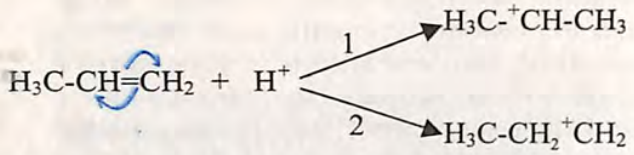
$$\text{(ii)}\ H_2C^+ - CH_3 + X^- \xrightarrow{\text{fast}} H_3C - CH_2 - X$$

In step (i), addition of proton (electrophile) to the double bond is slow, while step (ii) i.e. addition of nucleophile (X^-) to carbocation is fast. Any addition in which electrophile adds first is an electrophilic addition.

In case of unsymmetrical alkenes the addition takes place according to Markownikov rule, i.e. the more electronegative part of the addendum adds to that carbon which contains lesser number of hydrogen atoms. Thus, a molecule of HBr adds to propene in such a way that bromine adds to the central carbon atom which has lesser number of hydrogen atoms.

$$H_3C - CH = CH_2 + HBr \longrightarrow \underset{\text{2-Bromopropane}}{H_3C - CHBr - CH_3}$$

If we look at the structure of propene it has one methyl group attached to one of the doubly bonded carbons. In this case there are two possibilities of formation of carbocation in step (i) i.e. the proton either adds to terminal carbon (path 1) or to the central carbon (path 2).



The two carbocations are $(CH_3)_2{}^+CH$, a secondary(2°) carbocation, and $H_2C^+ CH_2 CH_3$, (1°) a primary carbocation.

We have studied in Unit 14 about the stability of carbocations. The secondary carbocation $H_3C\ C^+H\ CH_3$ a 2° carbocation is more stable than 1° carbocation, i.e. $H_3C\ CH_2\ C^+H_2$, therefore, the cation formed in step (i) i.e. H_3C-$^+$CH-CH_3 will be more stable and thus the nucleophile (negatively charged X:⁻) will add to the central carbon. It may be recalled (Unit 14) that tertiary carbocation (3°) is even more stable than the primary (1°) and secondary (2°) carbocations. Markownikov's rule can also be interpreted in terms of electronic interaction that is "electrophilic addition to a carbon-carbon double bond involves the intermediate formation of the more stable carbocation".

Decreasing order of reactivity of alkenes towards electrophilic addition is:
$R_2C = CR'_2 > R_2C = CHR' > R_2C = CH_2 \geq R - CH = CH - R > R - CH = CH_2 > CH_2 = CH_2 > CH_2 = CH - X$;
R and R' are alkyl groups and X is a halogen.

2. Addition of Sulphuric Acid : Cold, concentrated sulphuric acid adds to alkenes forming alkyl hydrogen sulphate, *e.g.*

$$H_2C{=}CH_2 + HOSO_2OH \longrightarrow H_3CCH_2OSO_2OH$$

3. Addition of halogen : Halogens (chlorine and bromine only) add, at ordinary temperature and without exposure to uv light to alkene to give vicinal dihalides,

$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} CH_2Br - CH_2Br$$

Red — 1,2-Dibromoethane (colourless)

This is a test for unsaturation, since the colour of bromine solution is decolourized.

Free radical addition : The addition of hydrogen bromide (not HCl and HI) to alkene in presence of benzoyl peroxide gives alkyl halide by anti-Markownikov addition. The effect was observed by Kharasch and hence is also called Kharasch effect. This is also known as peroxide effect.

$$CH_3 - CH = CH_2 + HBr \xrightarrow{(C_6H_5CO)_2O_2} CH_3 - CH_2 - CH_2Br$$

1-Bromopropane

In the absence of peroxide the addition is according to Markownikov rule. The reaction involves free radical and not carbocation mechanism. The peroxide effect is observed only for HBr and not for HCl and HI.

B. Miscellaneous Reactions

1. Hydroboration oxidation : Diborane adds to alkenes to give trialkyl borane, which on oxidation gives alcohol.The reaction has been shown below for propene,

The net addition is that of a water molecule, but it follows anti-Markownikov's addition.

The hydroboration was discovered by Herbert C. Brown, who was awarded Nobel Prize in 1980 for the tremendous synthetic uses of hydroboration.

2. Oxidation

(i) Dilute aqueous potassium permanganate at low temperature leads to formation of vicinal glycol.

$$H_2C = CH_2 + H_2O + O \xrightarrow[273K]{dil.KMnO_4} \underset{\displaystyle CH_2OH}{\overset{\displaystyle CH_2OH}{|}}$$

In presence of alkaline permanganate at elevated temperature alkenes undergo oxidative cleavage to form carboxylic acids or ketones depending on the nature of alkenes.

$$H_3C - CH = CH_2 + (BH_3)_2 \rightarrow H_3C - CH_2CH_2BH_2 \xrightarrow{H_3C-CH=CH_2} (H_3C - CH_2CH_2)_2BH$$

$$\downarrow\ CH_3 - CH = CH_2$$

$$B(OH)_3 + 3\ H_3C - CH_2CH_2OH \xleftarrow{H_2O_2/\bar{O}H} (H_3C - CH_2CH_2)_3B$$

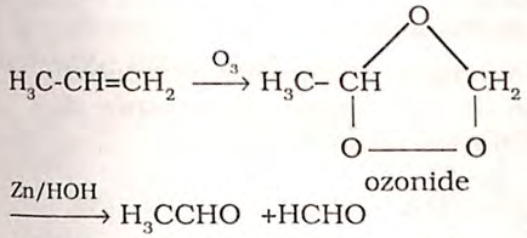
Boric acid — Alcohol

Reaction for propene

$$(H_3C)_2C=CH_2 \xrightarrow{KMnO_4/OH^-} (CH_3)_2C=O + CO_2 + H_2O$$

$$CH_3CH=CH\,CH_3 \xrightarrow{KMnO_4/OH^-} 2CH_3COO^-$$

3. Ozonolysis: Alkenes on reaction with ozone give ozonides, which undergo cleavage to yield carbonyl compounds. This reaction is used to locate the position of double bond in an alkene



$$\xrightarrow{Zn/HOH} H_3CCHO + HCHO$$

4. *Reduction* : Alkenes react readily with hydrogen in presence of finely divided nickel, platinum or palladium to give alkanes.

$$H_2C = CH_2 + H_2 \xrightarrow{Pt,\ Pd\ or\ Ni} H_3C - CH_3$$

5. *Polymerization* : Alkenes polymerize in presence of catalyst or at high temperature/ pressure.

$$nCH_2=CH_2 \xrightarrow{High\ temp./pressure} \{CH_2-CH_2\}_n$$

$$nH_3C-CH=CH_2 \xrightarrow{High\ temp./pressure} \left[\begin{array}{l} HC-CH_2 \\ \quad | \\ \quad CH_3 \end{array}\right]_n$$

Polypropene

The process of joining together, many simple molecules with double bond (monomers) to form a polymer is termed as "Polymerisation".

Example 15.11

An alkene with molecular formula C_7H_{14} gives propanone and butanal on ozonolysis. Write down its structural formula.

Solution

$CH_3CH_2CH_2CH = C(CH_3)_2$

15.3 ALKYNES

The hydrocarbons having carbon— carbon triple bond (C ≡ C) and general formula C_nH_{2n-2} are called **alkynes**. The simplest member of this class is ethyne C_2H_2. The *sp* hybridisation and nature of the C ≡ C bond has already been discussed in earlier units (6 and 14). Ethyne has a total of 3 σ-bonds and 2 π-bonds. The triple bond is made up of one σ-bond and two π-bonds. C_2H_2 is linear molecule in which the C ≡ C has a bond strength of 823 kJ mol^{-1} in ethyne. It is stronger than the C = C of ethene (678 kJ mol^{-1}) and C – C of ethane (370 kJ mol^{-1}).

15.3.1 Nomenclature

In IUPAC system the suffix -ane of the corresponding alkane is replaced by yne, *e.g.*

HC ≡ CH	$H_3C - C \equiv CH$
Ethyne	Propyne
$H_3C - C \equiv C - CH_3$	$H_3C - CH_2 - C \equiv CH$
But-2-yne	But-1-yne

The remaining rules of nomenclature are same as in case of alkanes and alkenes.

15.3.2 Acidity of Alkynes

Ethyne unlike ethene and ethane, reacts with sodium metal to form a salt, sodium ethynide and liberates hydrogen gas.

$$HC \equiv C - H + Na \longrightarrow HC \equiv C^-Na^+ + \tfrac{1}{2} H_2\uparrow$$

This reaction suggests the acidic character of H in ethyne. This is due to electronegativity of *sp* hybrid carbon. Among *sp*, sp^2 and sp^3 hybrid carbons the decreasing order of electronegativity is as follows: $sp > sp^2 > sp^3$. *sp* hybrid carbon has 50% 's' character, therefore the electrons of C – H bond are more closer to carbon and hydrogen shows appreciable acidity.

The relative acidity of acetylene is more than that of ammonia but less than that of water.

($H_2O > HC \equiv CH > NH_3$)

15.3.3 Preparation

1. From vicinal dihalides : Alkynes can be obtained through elimination reaction by dehydrohalogenation of a vicinal dihalide in presence of suitable base.

$$BrH_2C- CH_2Br \xrightarrow{Alc.\ KOH} H_2C = CH - Br \xrightarrow{NaNH_2} HC \equiv CH$$

A stronger base like sodamide is needed for the second step.

2. From tetrahalides : Alkyne is obtained, when a tetrahalide is heated with zinc.

$$Br_2HC - CHBr_2 + 2\ Zn \rightarrow HC \equiv CH + 2\ ZnBr_2$$

3. Industrial preparation : Ethyne is prepared by treating calcium carbide with water,

$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$
Calcium carbide

4. The lower alkynes can be converted to higher ones by reacting their alkynides with corresponding primary alkyl halides.

$$R - C \equiv CH + Na \xrightarrow{liq.NH_3} R - C \equiv C^- Na^+$$
Sodium alkynide

$$\xrightarrow{CH_3I} R\text{-}C \equiv C - CH_3 + NaI$$
Higher alkyne

15.3.4 Properties

Physical Properties

The physical properties of alkynes essentially follow the same trend as those of alkenes and alkanes. These are weakly polar. Alkynes are lighter than water and insoluble in water but soluble in organic solvents of low polarity *e.g.* carbon tetrachloride, benzene, ether etc. Their physical constants like m.p, b.p, and density show regular increase with increasing number of carbons and usual effects of branching.

Chemical Properties

***A. Acidic nature*:**

$$HC \equiv CH + Na \longrightarrow HC \equiv C^- Na^+ + \tfrac{1}{2} H_2$$
Sodium ethynide

$$\xrightarrow{Na} Na^+ - C \equiv C^- Na + \tfrac{1}{2} H_2$$
Disodium ethynide

The terminal alkynes react with heavy metal ions like Cu^+, Ag^+ in amoniacal solution to form insoluble alkynides.

$$R - C \equiv CH + Cu^+ \longrightarrow R - C \equiv C^- Cu^+ + H^+$$
Copper alkynide
(reddish brown)

$$R - C \equiv CH + Ag^+ \rightarrow R - C \equiv C^- Ag^+ + H^+$$
Silver alkynide
(white)

This reaction forms the basis of a diagnostic test to distinguish between terminal and non-terminal alkynes, purification of alkynes and separation of terminal alkynes from alkenes and alkanes.

***B. Addition reactions*:** All additions take place in two steps, first step leading to an alkene derivative to which further adds another molecule of addendum to yield the saturated product. Some representative addition reactions of alkynes are:

(i) Addition of halogens :

$$HC \equiv CH + Br_2 \rightarrow BrHC = CHBr + Br_2$$
$$\rightarrow Br_2HC - CHBr_2$$
1.1.2.2-Tetrabromoethane

(ii) Addition of hydrogen halides :

$$HC \equiv CH + HX \rightarrow XHC = CH_2 + HX$$
$$\rightarrow X_2HC - CH_3$$
1,1-Dihaloethane

(iii) Addition of hydrogen : Alkynes can be reduced to alkenes and then to alkanes in presence of catalyst, specially palladium/charcoal

$$HC \equiv CH + H_2 \xrightarrow{Pd/C} H_2C = CH_2 + H_2 \rightarrow H_3C - CH_3$$

(iv) Addition of water : Alkynes add one molecule of water in presence of sulphuric acid and mercuric sulphate to yield a carbonyl compound, *e.g.*

$$HC \equiv CH + H_2O \xrightarrow[H_2SO_4]{Hg^{2+}/HgSO_4} \underset{\text{Unstable}}{\overset{OH}{\overset{|}{HC}} = CH_2} \rightarrow H_3CCHO$$

$$RC \equiv CH + H_2O \xrightarrow[H_2SO_4]{Hg^{2+}/HgSO_4} \overset{OH}{\overset{|}{RC}} = CH_2 \rightarrow RCOCH_3$$

(v) Reactions with alcohols, hydrogen cyanide and carboxylic acids (vinylation): Ethyne adds a molecule of alcohol in the presence of alkali to give vinyl ether,

$$HC \equiv CH + CH_3OH \xrightarrow[393-453\ K]{KOH} H_3CO\text{-}HC = CH_2$$
Methyl vinyl ether

With HCN, ethyne gives vinyl cyanide,

$$HCN + HC \equiv CH \rightarrow H_2C = CH\text{-}CN$$
Vinyl cyanide

Similarly alkynes add acids in the presence of a Lewis acid catalyst or Hg^{++} ions to give vinyl esters *e.g.*

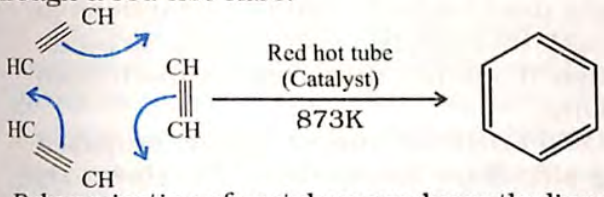
$$H - C \equiv CH + H_3CCOOH \xrightarrow{Hg^{++}/353K}$$

$$CH_3 - \overset{O}{\overset{\|}{C}} - O - CH = CH_2$$
Vinyl ethanoate

$$R-C\equiv CH + H_3CCOOH \xrightarrow{BF_3} CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{R}{|}}{C}=CH_2$$

α-alkylvinyl ethanoate

(vi) Polymerization : The tendency to polymerize is less in alkynes than in alkenes, therefore, these give low molecular mass polymers. Ethyne can polymerize to give benzene when passed through a red hot tube.



Polymerization of acetylene produces the linear polymer *polyacetylene*. It is a high molecular weight conjugated polyene containing repeating units $(-CH = CH - CH = CH-)_n$. Under proper conditions this material conducts electricity. Thin films of polyacetylene can be used as electrodes in batteries. Having much higher conductance than metal conductors, lighter and cheaper, batteries can be made from it.

Example 15.8

How would you separate propene from propyne?

Solution

By passing the mixture through a solution of ammoniacal silver nitrate, propyne will precipitate out as silver propynide and propene will pass unchanged.

$$H_3C-C\equiv CH + Ag^+ \longrightarrow \underset{\text{(precipitate)}}{H_3C-C\equiv C^- - Ag^+}$$

15.4 ALKADIENES

The name alkadiene is often shortened as diene. These are unsaturated hydrocarbons having two carbon – carbon double bonds per molecule. The general formula of alkadiene is similar to alkyne C_nH_{2n-2}, hence these are isomeric with alkynes. The dienes may be of three types depending on the position of double bonds.

1. Isolated dienes : The double bonds are separated by more than one single bond, *e.g.*

$CH_2 = CH - CH_2CH_2 - CH = CH_2$
Hexa-1, 5-diene

2. Cumulated dienes : The double bonds between successive carbon atoms are called cumulated double bonds, *e.g.*

$CH_2 = C = CH_2$
Propa-1, 2-diene (Allenes)

$CH_3 - CH = C = CH - CH_3$
Penta-2, 3-diene (Dimethyl allene)

3. Conjugated dienes : The dienes in which double bond is alternate with single bond are called conjugated dienes, *e.g.*

$CH_2 = CH - CH = CH_2$
Buta-1, 3-diene

Among these three types of dienes the conjugated dienes are the most important because these are the most stable and show strikingly different properties.

Resonance imparts stability to butadiene or any other conjugated system.

The pi electrons of a conjugated diene are not localized between a pair of adjacent carbons as in a simple alkene. Instead, pi electron density is delocalized over the entire diene unit, making it more stable and giving partial double bond character between carbon atoms 2 and 3 of butadiene.

15.4.1 Properties

The nonconjugated dienes behave exactly in the same way as simple alkenes except that the attacking reagent is consumed in twice the amount required for one double bond. But due to mutual interaction of double bonds, i.e. delocalisation of electrons in conjugated dienes, their properties are entirely different.

Electrophilic Addition : 1, 3-butadiene and HBr taken in equimolar amounts yield two products, 3-bromo-but-1-ene and 1-bromo-but-2-ene through 1, 2 and 1,4 addition respectively.

$CH_2 = CH - CH = CH_2 + HBr \rightarrow$

$H_3C - CHBr - CH = CH_2$ +
3-Bromo-but-1-ene (1,2-addition)

$H_3C - HC = CH - CH_2Br$
1-Bromo-but-2-ene (1,4-addition)

The resonating structures of the intermediate carbocation, formed after addition of the electrophile i.e. H^+, can add the anion in two alternative ways (path a or path b) to yield 1,2 and 1,4 addition products.

$H_3C\text{-}\overset{+}{C}H\text{-}CH{=}CH_2 \leftrightarrow H_3C\text{-}CH{=}CH\text{-}\overset{+}{C}H_2$

$\downarrow a \qquad\qquad \downarrow b$

$H_3C\text{-}\underset{\displaystyle Br}{\underset{|}{CH}}\text{-}CH = CH_2 \qquad H_3C\text{-}CH{=}CH\text{-}CH_2Br$

Example 15.9

A conjugated alkadiene having molecular formula $C_{13}H_{22}$ on ozonolysis yielded ethyl methyl ketone and cyclohexanal. Identify the diene, write it's structural formula and give its IUPAC name.

Solution

Two products *viz.* ethyl methyl ketone, $H_3CCOC_2H_5$ and cyclohexanal, $C_6H_{11}CHO$ are obtained on ozonolysis. The two termini of the alkadiene would be

$H_3C\diagdown\ \diagup H$ $\quad$ and $\quad$ $= CH - C_6H_{11}$

$H_3C - H_2C\diagup\ \diagdown C =$

After arranging these in conjugation we conclude the structure as,

$H_3C\diagdown\ \quad\quad\ \diagup H$

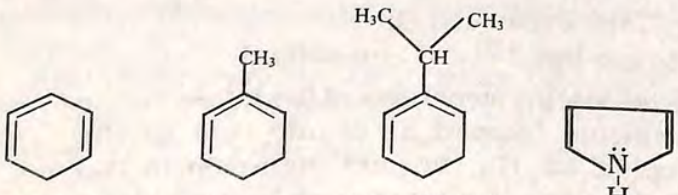
$\quad\ C = CH - CH = C$

$H_3C\text{-}H_2C\diagup\ \quad\quad\ \diagdown C_6H_{11}$

IUPAC name: 1-cyclohexyl-4-methylhex-1, 3-diene.

15.5 AROMATIC HYDROCARBONS

The term aromatic (Greek; aroma means fragrance) was first used for compounds having pleasant odour although the structure was not known. Now the term aromatic is used for a class of compounds having a characteristic stability despite having unsaturation. These may have one or more benzene rings (benzenoid) or may not have benzene ring (non-benzenoid). Benzenoid compounds include benzene and its derivatives having aliphatic side chains (arenes) or polynuclear hydrocarbons, eg. naphthalene, anthracene etc.



Benzene | Toluene | Isopropyl benzene (Cumene) | Pyrrole

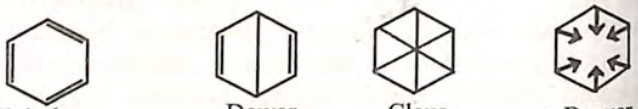
15.5.1 Nomenclature

The nomenclature of aromatic compounds has already been discussed in Unit 14.

15.5.2 Structure of Benzene

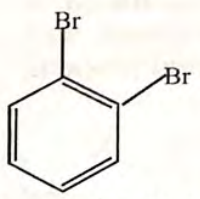
Benzene has been known since 1825 when it was first isolated by Michael Faraday. From elemental analysis and molecular mass determination, it was found that the molecular formula of benzene is C_6H_6, indicating high unsaturation. However, benzene does undergo addition reactions in contrast to unsaturated hydrocarbons, although it mainly undergoes substitution reactions.

In 1865 Friedrich August Kekulé proposed a ring structure for benzene (I). However, many alternative structures have been proposed from time to time by different workers. (II – IV).

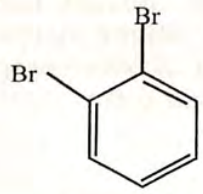


Kekule (1865) (I) | Dewar (1867) (II) | Claus (1867) (III) | Baeyer (1892) (IV)

The main objection against Kekulé structure was that it should yield two ortho disubstituted products when it reacts with bromine. However, experimentally benzene was found to yield only one product.



(Two bromine atoms are attached to carbons joined together through a double bond)



(Two bromine atoms are attached to carbons joined together through a single bond)

Kekulé removed this objection by proposing that the double bonds in benzene are continuously oscillating back and forth between two adjacent positions. Since positions of double bonds are not fixed, only one product is formed. This structure came to be known as Kekulé's dynamic formula, which formed the basis for the present electronic structure of benzene.

Friedrich August Kekulé,a German chemist was born in 1829 at Darmsdt in Germany.He became Professor in 1856 and Fellow of Royal Society in 1875.He made major contribution to structural organic chemistry by proposing in 1858 that carbon atoms can join to one another to form chains and later in 1865,he found an answer to the challenging problem of benzene structure by suggesting that these chains can close to form rings.He gave the dynamic structural formula to benzene which forms the basis for its modern electronic structure.He described the discovery of benzene structure later as:

FRIEDRICH AUGUST KEKULÉ (7th September 1829–13th July 1896)

"I was sitting writing at my text book,but the work did not progress; my thoughts were elsewhere.I turned my chair to the fire,and dozed.Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background.My mental eye, rendered more acute by repeated visions of this kind , could now distinguish larger structures of manifold conformations; long rows,sometimes more closely fitted together; all twisting and turning in snake like motion.But look! What was that? One of the snakes had seized hold of it's own tail,and the form whirled mockingly before my eyes.As if by a flash of lightening I woke;....I spent the rest of the night working out the consequences of the hypothesis.Let us learn to dream, gentlemen, and then perhaps we shall learn the truth but let us beware of making our dreams public before they have been approved by the waking mind."(1890).

One hundred years later, on the occasion of Kekulé's centenary celebrations a group of compounds having polybenzenoid structures have been named as Kekulenes.

Modern Concept

Stability of benzene (Resonance)

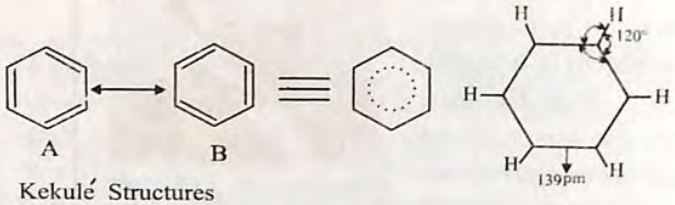
Benzene resists addition whereas it readily undergoes substitution reactions, like nitration, halogenation etc. This indicates that benzene is more stable than the hypothetical cyclohexatriene moleucle. This has been proved by the fact that the enthalpies of hydrogenation and combustion of benzene are lower than expected. *Enthalpy of hydrogenation is the change in enthalpy when one mole of an unsaturated compound is hydrogenated.* It has been found experimentally that enthalpy of hydrogenation for disubstituted alkenes, R-CH=CH-R varies between 117-125 kJ mol^{-1}. Accordingly, the values for cyclohexene and cyclohexa-1, 3-diene and hypothetical cyclohexa –1,3,5-triene were calculated and compared with their experimental values.

While the experimental values of enthalpy of hydrogenation for cyclohexene is as expected, the variation in case 1,3 cyclohexadiene is small and is due to delocalization. The value of enthalpy of hydrogenation of benzene is much higher than the corresponding calculated value for hypothetical 1,3,5 - cyclohexatriene indicating that benzene does not have this type of structure.

X-ray studies show that it is a planar molecule and that all six C-C bonds in benzene are of equal length (139 pm), intermediate between C-C single bond (154 pm) and C=C (134 pm). All six carbons are sp^2 hybridized and all bond

Compound	Enthalpy of hydrogenation (kJ mol^{-1})	
	Experimental Value	Calculated Value
Cyclohexene	-119.5	-119.5
1,3-Cyclohexadiene	-232.8	-239.0
1,3,5-Cyclohexatriene	-	-358.5
Benzene	-208.1	-

angles are 120° as discussed in Unit 14. Benzene is a hybrid of various resonating structures, the two Kekulé structures A and B, being the main contributing forms.



Kekulé Structures

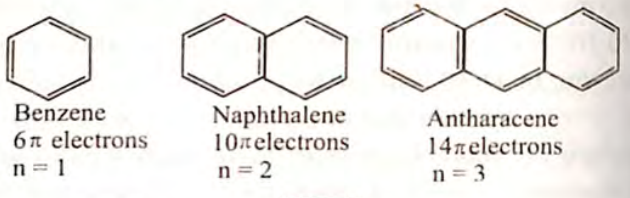
15.5.3 Aromaticity in Benzene and Related Systems

After the structure of benzene was established, the term aromatic was adapted for such compounds which despite having π bonds (unsaturation) resist addition and instead undergo substitution. The aromaticity in benzene is attributed to the six delocalised pi electrons in the coplanar carbon hexagon. When a bonding orbital is not restricted to two atoms but is spread over more than two atoms, *e.g.* six in benzene, such bonding orbitals are said to be delocalised. Delocalisation results in greater stability.

The modern theory of aromaticity was advanced by Eric Hückel in 1931. Aromaticity is a function of electronic structure. Any polynuclear compound, heterocyclic rings or cyclic ions may be aromatic if these have a specific electronic structure. The important features of the theory are,

1. ***Delocalization*** : Complete or ample delocalization of π electrons of the ring system is a necessary requirement for aromatic character.
2. ***Planarity*** : Ample delocalisation of π-electrons is possible only if the ring is planar to allow cyclic overlap of p-orbitals, thus benzene is aromatic but cyclooctatetrane is not, since the latter is not planar.

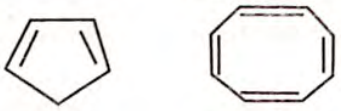
Hückel's rule or (4n + 2) rule: The rule states that in a conjugated, planar, cyclic system if the number of delocalized π-electrons is (4n+2) n being an integar, i.e. 1,2,3, etc. it will be aromatic, otherwise not. Benzene, naphthalene, anthracene and phenanthrene are aromatic as they contain (4n + 2), i.e. 6,10,14, π electrons in a conjugated cyclic arrary. The cyclopentadiene and cyclooctatetraene are non-aromatic as instead of (4n +2) π e^- these have 4n π e^-. Moreover,they are non-planar.



Benzene
6π electrons
n = 1

Naphthalene
10π electrons
n = 2

Antharacene
14π electrons
n = 3



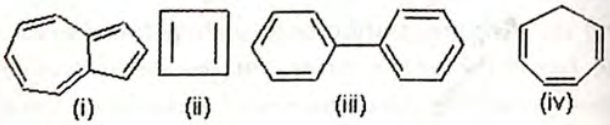
$4\pi e^-$ $8\pi e^-$

Cyclopentadiene Cyclooctatetraene

Non-aromatic cyclic hydrocarbons

Exercise 15.7

Predict which of the following systems would be aromatic and why?



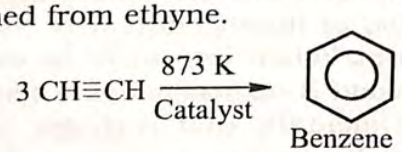
(i) (ii) (iii) (iv)

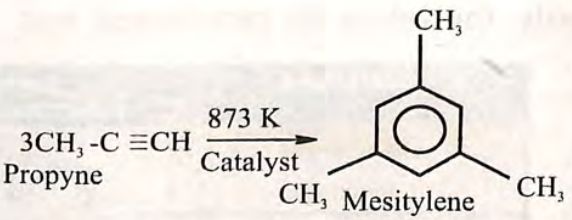
Answer

(i) and (iii). According to Hückel's rule, these two only are (4n+2) systems, (ii) is a 4 n system (iv) is 4 n + 2 system but devoid of conjugation due to a sp^3 carbon.

15.5.4 Preparation of Benzene and its Homologues

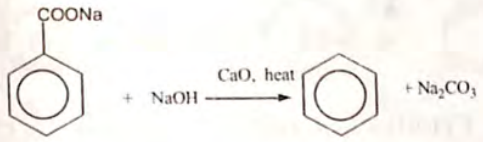
(i) From alkynes : Alkynes polymerize at high temperatures to yield arenes *e.g.* benzene is obtained from ethyne.



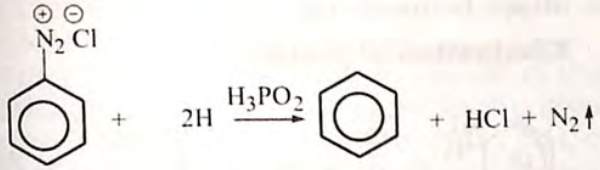


(ii) Decarboxylation of aromatic acids : In laboratory benzene is prepared by heating

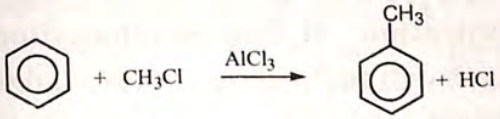
sodium benzoate with sodalime.



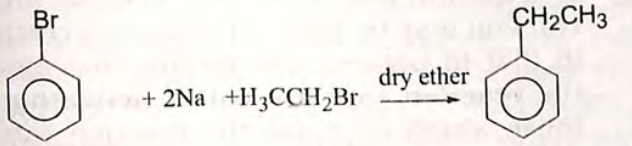
(iii) Reduction of diazonium salts : In presence of hypophosphorus acid, benzene diazonium chloride is converted into benzene (diazo group is replaced by H).



(iv) Friedel-Crafts reaction : Benzene can yield arenes on treating with alkyl halide in presence of anhydrous aluminium chloride.

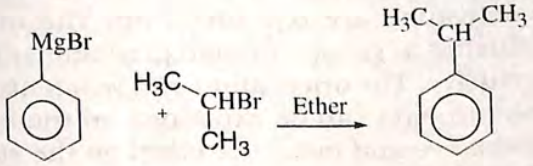


(v) Wurtz–Fittig reaction : Arenes can be obtained by action of sodium metal on a mixture of aryl halide and alkyl halide in ether.



Ethylbenzene

(vi) From Grignard reagents : Arenes can be prepared by reacting Grignard reagent with alkyl halide, *e.g.*



Isopropyl benzene

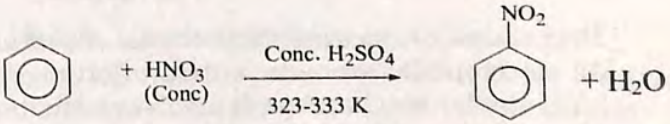
15.5.5 Properties

Physical Properties : Aromatic hydrocarbons are usually colourless, insoluble in water but soluble in organic solvents. They are inflammable, burn with sooty flame and have a characteristic odour. They are toxic and carcinogenic in nature. Their boiling points increase with increasing molecular mass.

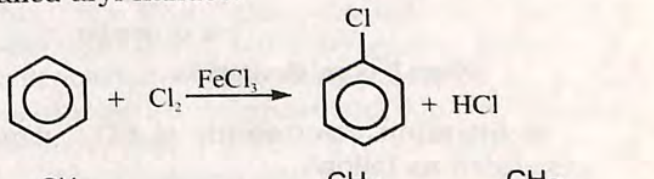
Chemical Properties : The characteristic reactions of benzene and benzenoid compounds are electrophilic substitution reactions, however under special conditions these also undergo addition and oxidation reactions.

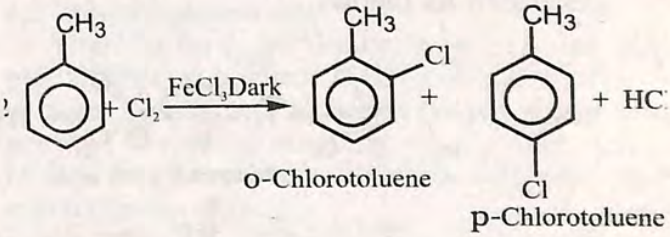
(i) Electrophilic substitution reactions : The important electrophilic substitution reactions are nitration, halogenation, sulphonation, Freidel - Craft alkylation and acylation.

(a) Nitration : The nitration of benzene is carried out with a mixture of concentrated nitric acid and conc. H_2SO_4 (nitrating mixture).



(b) Halogenation : Benzene and its homologues react with halogens (Cl_2, Br_2 etc) in the presence of a Lewis acid e.g. $FeCl_3$/$FeBr_3$ as catalyst to yield halogen substituted products, commonly called aryl halides.

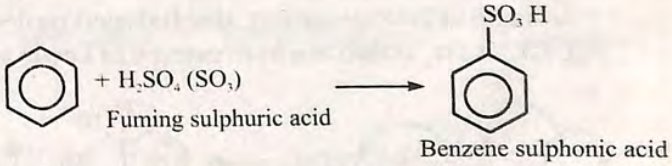




o-Chlorotoluene

p-Chlorotoluene

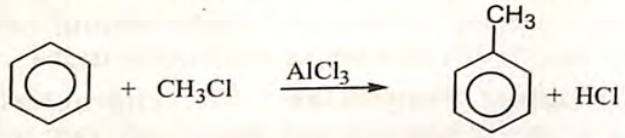
(c) Sulphonation : The sulphonation of benzene is carried out by heating it with fuming sulphuric acid,



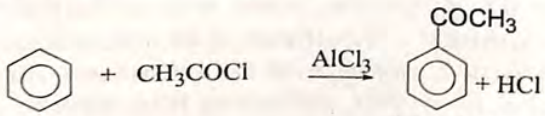
Benzene sulphonic acid

(d) Friedel-Crafts reaction (alkylation) : The reaction of benzene with alkyl halide in presence

of a Lewis acid as catalyst to get alkyl benzene is called Friedel Crafts alkylation.For example,

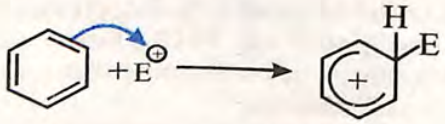


Friedel-Crafts reaction(acylation) : The reaction of benzene with an acyl halide or acid anhydride in presence of Lewis acid as catalyst to give acylbenzene (ketone) is called Friedel-Craft acylation.For example,



Acetophenone

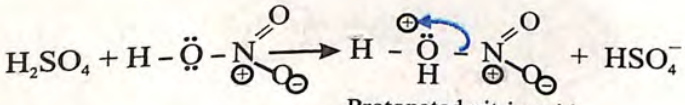
Mechanism of electrophilic aromatic substitution: All electrophilic aromatic substitution reactions have similar mechanism. It involves formation of a σ - complex, followed by elimination of a proton,



σ -Complex

where $\overset{\oplus}{E}$ is an electrophile

In nitration electrophile is NO_2^+, which is generated as follows,



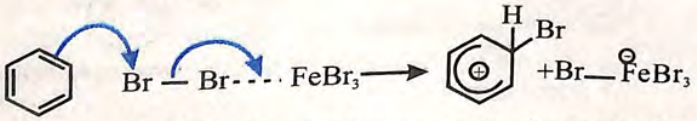
Protonated nitric acid

$$H_2O + O = \overset{\oplus}{N} = O$$

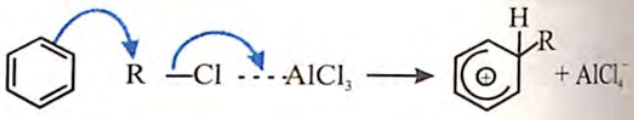
Nitronium ion

In sulphonation, fuming sulphuric acid has SO_3 which acts as an electrophile.

In case of halogenation, the halogen molecule e.g. Cl_2 or Br_2 polarizes in presence of Lewis acid,



In Friedel-Crafts alkylation, a similar complex is formed by polarization of the alkyl halide molecule,

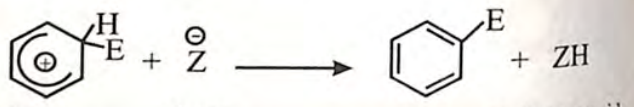


In Friedel – Crafts acylation, $\overset{\oplus}{R}CO$ is the electrophile,

$$RCOCl + AlCl_3 \longrightarrow R\overset{\oplus}{C}O\,A\overset{\ominus}{l}Cl_4$$

A 1: 1 complex between RCOCl and Lewis catalyst may also be formed which can directly attack benzene ring,

Elimination of proton



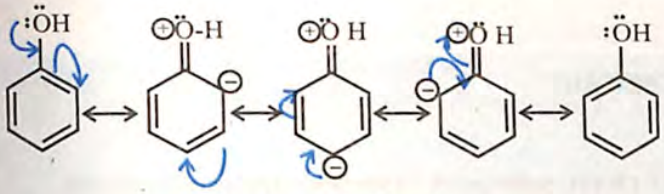
sigma complex — base — conjugate acid

$\overset{\ominus}{Z} = Fe\overset{\ominus}{X}_4 (X = Cl, Br)$ in halogenation; $\overset{\ominus}{H}SO_4$ in nitration; H_2O(in sulphonation) and $Al\overset{\ominus}{X}_4 (X = Cl, Br)$ Friedel – Crafts alkylation/ acylation.

15.5.6 Orientation in Benzene Ring

The susbstituent already present in the benzene ring directs the incoming group either to *ortho* and *para* or to *meta* position and the reaction may be faster or slower as compared to that in benzene.The groups that increase the reaction rate are called activating and those which decrease the reaction rate are deactivating. The former are generally *o,p* directing and increase electron density on the ring while the latter are *m*-directing and decrease the overall electron density on the benzene ring.There is a third category of groups,e.g. halogens which though deactivating are *o,p*- directing. The directive influence of groups though predominent is not exclusive. The orientation and reactivity of the substituents can be explained on the basis of resonance and inductive effect on the stability of the intermediate arenium ions formed during electrophilic substitution.

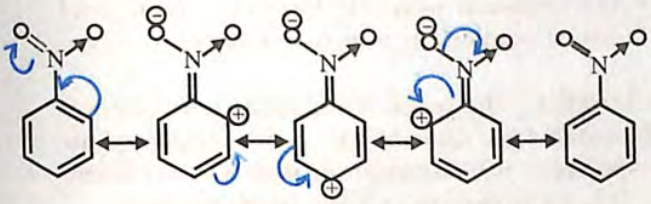
As an example we shall discuss the orientation effect of -OH (phenolic) which is *o*- and *p*- directing and $-NO_2$ which is *m*-directing. Let us see their effects on the stability of arenium ions.



Resonance in Phenol

In case of phenol, the overall electron density on the benzene ring increases vis-à-vis benzene, stabilising the arenium ion by neutralising some of its positive charge. Since the electron density is more concentrated on the two *o*- and *p*-positions, the substitution is mainly in these positions. Other examples of *o,p*-directing groups are $-NH_2$, -NHR, $-NR_2$, $-OCH_3$ and CH_3, C_2H_5 etc.

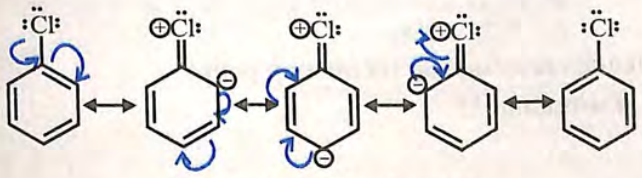
Let us take nitro ($-NO_2$) group as an example of deactivating and *m*-directing group.



Resonance in Nitrobenzene

In this case the overall electron density on benzene ring decreases (deactivation) and this destabilises the arenium ion by further increase in positive charge. Here the electron density on the *o*- and one *p*-position is comparatively less and therefore the two *meta* positions are relatively rich in electron density, thus resulting in *m*-substitution. Other important examples of *m*-directing groups are -COOH, $-SO_3H$, -CN, -CHO,-COR etc.

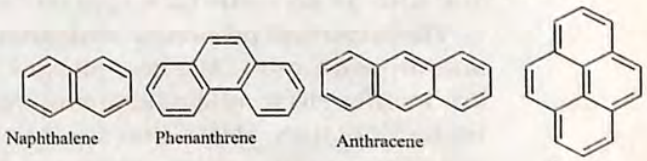
In case of aryl halides halogens are highly deactivating because of their strong (negative inductive) I-effect. Therefore overall electron density on benzene ring decreases.However, due to resonance the electron density on *o*- & *p*-positions is more,therefore, these are *o,p*-directing.As an example,let us look at the resonating structures of chlorobenzene,



Resonance in Chlorobenzene

15.5.7 Polynuclear Hydrocarbons

The main source of polynuclear hydrocarbons is coal tar. Naphthalene is the largest single constitutent (6 – 10%) of coal tar, obtained by cooling the middle oil fraction. (b.p. 443–503 K) of coal tar. Anthracene is obtained from green oil fraction (b.p. 543–633 K) of coal tar in about 1% yield. The polynuclear hydrocarbons are made up of 2 or more aromatic rings which can be linear like naphthalene and anthracene or angular like phenanthrene and pyrene.

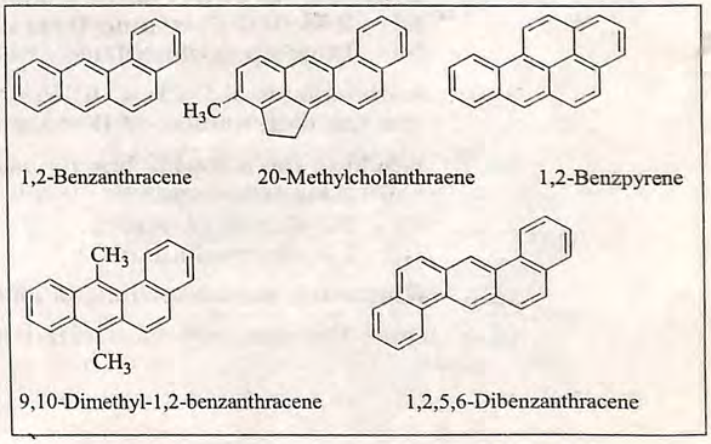


Naphthalene Phenanthrene Anthracene Pyrene

15.5.8 Carcinogenicity and Toxicity

Most polynuclear hydrocarbons have carcinogenic property. It was noticed that people working under prolonged exposure to coal tar tend to suffer from skin cancer. A group of British chemists first noticed that high boiling fluorescent fraction of coal tar was responsible for producing cancer. The major component of this fraction was found to be 1,2-benzanthracene. Later on, many polynuclear hydrocarbons were discovered to be potent carcinogenic compounds *e.g.* 20-methyl-cholanthrene, 1,2-benzpyrene, 9,10-dimethyl-1,2-benznthracene etc.

There is no general rule by which one can predict the carcinogenic activity of hydrocarbons or their derivatives. However, the number and position of some groups e.g. $-CH_3$, -OH, -CN, $-OCH_3$, etc. have been found to influence the carcinogenic activity.



1,2-Benzanthracene 20-Methylcholanthraene 1,2-Benzpyrene

9,10-Dimethyl-1,2-benzanthracene 1,2,5,6-Dibenzanthracene

SUMMARY

The hydrocarbons are classified as open chain saturated (alkanes) and unsaturated (alkenes,polyenes and alkynes), cyclic (alicyclic) and aromatic, according to their structure. Hydrocarbons are mainly obtained from petroleum, which is the major source of commercial energy. Petrochemicals are the prominent starting materials used for the manufacture of a large number of commercially important products. LPG (liquified petoleum gas) and CNG (compressed natural gas), the main source of energy for automobile industry and also as domestic fuels, are obtained from petroleum.

The important properties of alkanes are free radical substitution, combustion, oxidation and aromatization. Alkenes, alkynes and alkadienes undergo addition reactions, which are mainly electrophilic additions. Aromatic hydrocarbons despite having unsaturation undergo mainly electrophilic substitution. These undergo addition and nucleophilic substitution only under special conditions.

Alkanes show conformational isomerism due to free rotation along the C-C sigma bonds. However, cyclohexane exists in different conformational isomeric forms i.e. chair and boat forms Alkenes exhibit geometrical (*cis-trans*) isomerism due to restricted rotation around the double bond.

Benzene and benzenoid compounds show aromatic character. Aromaticity is a function of specific electronic structure symbolized by Hückel (4n+2) rule. The nature of groups or substituents attached to benzene ring is responsible for activation or deactivation of the ring towards electrophilic substitution and also for orientation of the incoming group.

Some of the polynuclear hydrocarbons having a number of condensed benzene rings have carcinogenic property.

EXERCISES

15.1 Write IUPAC names for the following molecules,

(a) $CH_2=\underset{\displaystyle H}{\underset{|}{C}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH-CH=CH_2$ (b) $HC\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2$

15.2 Draw the structures of the following, showing all C and H atoms.

(a) 2-Methyl -3-isopropylheptane

(b) Dicyclopropylmethane

15.3 In the alkane $H_3C-CH_2-C-(CH_3)_2-CH_2-CH(CH_3)_2$, identify $1^0,2^0,3^0$ carbon atoms and give the total number of H atoms bonded to each one of these.

15.4 Which of the following has the highest boiling point?

(i) 2-methylpentane

(ii) 2,3-dimethylbutane

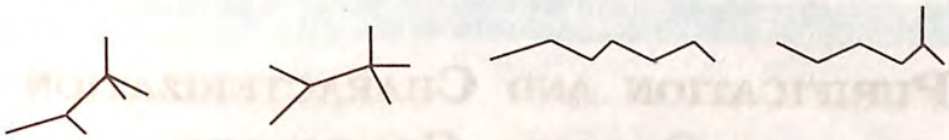
(iii) 2,2-dimethylbutane

15.5 What effect does branching of an alkane chain has on its melting point?

15.6 Draw Newman projection formulae of n-butane.

15.7 Why propane has only one eclipsed conformation while butane has three? Explain and give diagrams.

15.8 Arrange the following in increasing order of their release of energy on combustion:



(i) (ii) (iii) (iv)

15.9 Draw the structures of three cycloalkane isomers with molecular formula C_5H_{10}, each with a different size ring.

15.10 Between the two conformational isomers of cyclohexane,i.e. chair and boat forms, which one is more stable and why?

15.11 Some fuels have octane numbers higher than 100.Explain.

15.12 Draw structures of the six isomeric pentenes,C_5H_{10}.Specify as *E* or *Z* to each geometric isomer.

15.13 Why alkynes undergo nucleophilic addition reactions while simple alkenes do not?

15.14 Addition of HBr to propene yields 2-bromo propane,while in presence of benzoyl peroxide the same reaction yields 1-bromopropane.Explain and give mechanism.

15.15 Why conjugated dienes undergo 1,4-additions? Explain.

15.16 If one mole of HBr is added to the following compounds,write down the structures of the product/products expected to be formed. (i) Buta-1, 3-diene (ii) Penta-1, 3-diene (iii) Penta-1, 4-diene (iv) But-1-ene

15.17 How would you carry out the following conversions?

(i) $H_3C\text{-}CH_2\text{-}CH{=}CH_2 \rightarrow H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$

(ii) $H_3C\text{-}CH_2\text{-}CH{=}CH_2 \rightarrow H_3C\text{-}CH_2\text{-}CH(OH)\text{-}CH_2OH$

(iii) $Br_2\text{-}CH\text{-}CHBr_2 \rightarrow HC{\equiv}CH$

(iv) $H_3CC{\equiv}CH \rightarrow H_3CCOCH_3$

15.18 Write down the products of ozonolysis of 1,2-dimethylbenzene (o-xylene).How does the result support Kekule structure for benzene?

15.19 Account for the following order of acidity, Acetylene>Benzene>Hexane.

15.20 What are the necessary conditions for any compound to show aromaticity?

15.21 Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

15.22 Write down the products and give the mechanism of the following reactions.

(i) $C_6H_5OH + H_2SO_4$(conc.)

(ii) $C_6H_5CH_3 + HNO_3$ and H_2SO_4(conc.)

15.23 Which of the following polymerizes most readily and why?
(i) Acetylene (ii) Ethene (iii) Buta-1, 3-diene

15.24 How would you convert the following compounds to benzene?
(i) Acetylene (ii) Benzoic acid (iii) Hexane (iv) Benzene diazonium chloride

15.25 Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

15.26 Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+

(i) chlorobenzene,2,4-dinitrochlorobenzene, p-nitrochlorobenzene

(ii) toluene, $p\text{-}H_3C\text{-}C_6H_4\text{-}CH_3$, $p\text{-}H_3C\text{-}C_6H_4\text{-}NO_2$,$p\text{-}O_2N\text{-}C_6H_4\text{-}NO_2$.

UNIT 16

PURIFICATION AND CHARACTERIZATION OF ORGANIC COMPOUNDS

Objectives

After studying this Unit, you will be able to

- learn the principles of different methods of purification of organic compounds.
- know about the chemical reactions involved in qualitative analysis of different elements (N,S,P and halogens) present in an organic compound.
- understand the chemistry of quantitative analysis of elements present in an organic compound.
- learn the methods for determination of molecular masses of organic compounds.
- learn the principle of mass spectrometry.
- derive empirical and molecular formulae and calculate molecular mass of an organic compound from a given data.

In Units 14 and 15, we have learnt that the properties of organic compounds can be correlated to their structures. In other words, the structures of compounds help us to understand their chemistry. The determination of structure of an organic compound involves the following steps:

(i) Purification of the compound,
(ii) Qualitative analysis for determining the elements present,
(iii) Quantitative analysis of elements detected under (ii),
(iv) Determination of Molecular mass, and
(v) Determination of structural formula by physicochemical and spectroscopic methods.

In this unit, we shall learn the principles of the processes involved in steps i-v. The physicochemical and spectroscopic methods (step v) are not discussed in detail in this unit. You will learn more about these methods in higher classes.

16.1 PURIFICATION

Before investigating the structure and properties of an organic compound, it is essential to obtain the compound in its purest form. Various methods used for purification are based on the nature of the compound and the impurity present in it. The common techniques used for purification are as follows;

(i) Filtration,
(ii) Recrystallization,
(iii) Sublimation,
(iv) Distillation,
(v) Differential extraction, and
(vi) Chromatography.

Finally, the purity of the compound is checked by determining its melting or a boiling point. Most of the pure compounds have sharp melting and boiling points. New methods of checking the purity of a compound are based on different types of chromatographic and spectroscopic techniques.

16.1.1 Filtration

Filtration is used to separate an insoluble solid component of the mixture from the soluble component in a given solvent.

For example, a mixture containing naphthalene and urea can be separated by this technique. Urea dissolves in water while naphthalene remains insoluble. Urea is recovered from the filtrate by evaporating water.

Sometimes for separation purposes the filtration of a hot solution is required (Fig. 16.1). For example, a mixture of anthracene and benzoic acid is separated by dissolving it in hot water and filtering the hot solution. Benzoic acid crystallizes on cooling, while anthracene remains as an insoluble residue.

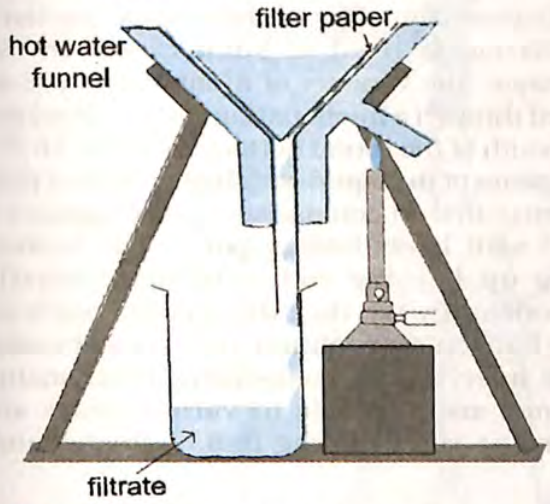


Fig.16.1 *Filtration of hot mixture. The funnel is kept hot by hot water*

At times, the process of filtration is very slow and takes a long time. In such cases, filtration is carried out under reduced pressure using a Büchner funnel and a filter pump (Fig.16.2).

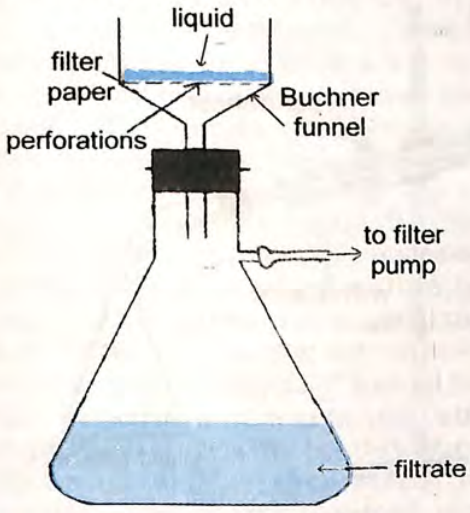


Fig.16.2 *Filtration under reduced pressure.The pressure in filtration flask is reduced with water pump/vacuum pump.*

16.1.2 Recrystallization

This is one of the most commonly used techniques of purification of solid organic substances. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get nearly a saturated solution. On cooling, the pure substance crystallizes out and is removed by filtration. The filtrate (mother liquor) contains impurities and small quantity of the compound. If the substance is highly soluble in one solvent and too little soluble in another solvent, then crystallization can be satisfactorily carried out in a mixture of these solvents taken in an appropriate proportions. Coloured impurities, if present, are removed by activated charcoal. Repeated crystallizations become necessary for purifying substance containing impurities of comparable solubilities.

16.1.3 Sublimation

On heating, some solid substances change from solid to vapour state without passing through liquid state. Such substances are known as sublimable. Sublimation is used to separate sublimable volatile compounds from non-sublimable impurities. The impure compound is heated in a porcelain dish covered with a filter paper which is perforated with a number of small holes. A funnel with its stem plugged with cotton is inverted over the porcelain dish (Fig.16.3). The vapours of the pure compound get deposited on the inner side of the funnel. Compounds like camphor and naphthalene can be purified by this method.

16.1.4 Distillation

This important method is used to separate (i) volatile liquids from non-volatile impurities and (ii) liquids having sufficient difference in their boiling points. Liquids having different boiling points vaporize at different temperatures. The vapours are cooled and the liquids so formed are collected separately. Chloroform (b.p. 334 K) and aniline (b.p.457 K) are easily separated by distillation (Fig. 16.4). The liquid mixture is taken

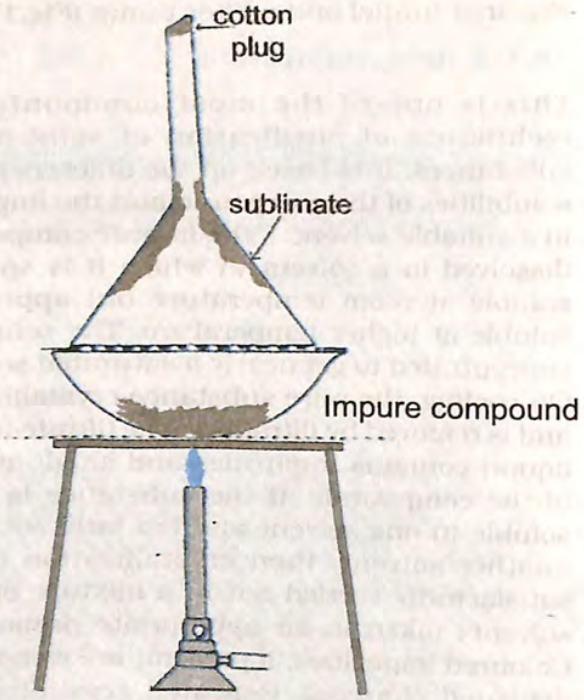


Fig.16.3 *Sublimation. The vapours of the volatile component are deposited over the inner surface of funnel.*

in a round bottom flask and heated carefully. On boiling, the vapours of lower boiling component are formed first. The varpours are condensed using a condenser and the liquid formed is collected in the receiver. The vapours of higher boiling component form later and upon condensation, the liquid is collected separately.

Fractional Distillation: If the difference in boiling points of two liquids is not much, simple distillation cannot be used to separate them. The vapours of such liquids are formed within the same temperature range and are condensed simultaneously. The technique of fractional distillation is used in such cases. In this technique, the vapours of a liquid mixture are passed through a fractionating column fitted over the mouth of the round bottom flask (Fig. 16.5).

Vapours of the liquid with higher boiling point condense first in comparison to the vapours of liquid with lower boiling point. The vapours rising up become richer in more volatile component. By the time the vapours reach top of the fractionating column, they consist mainly of the more volatile component. Fractionating columns are available in various sizes and designs as shown in Fig. 16.6. A fractionating

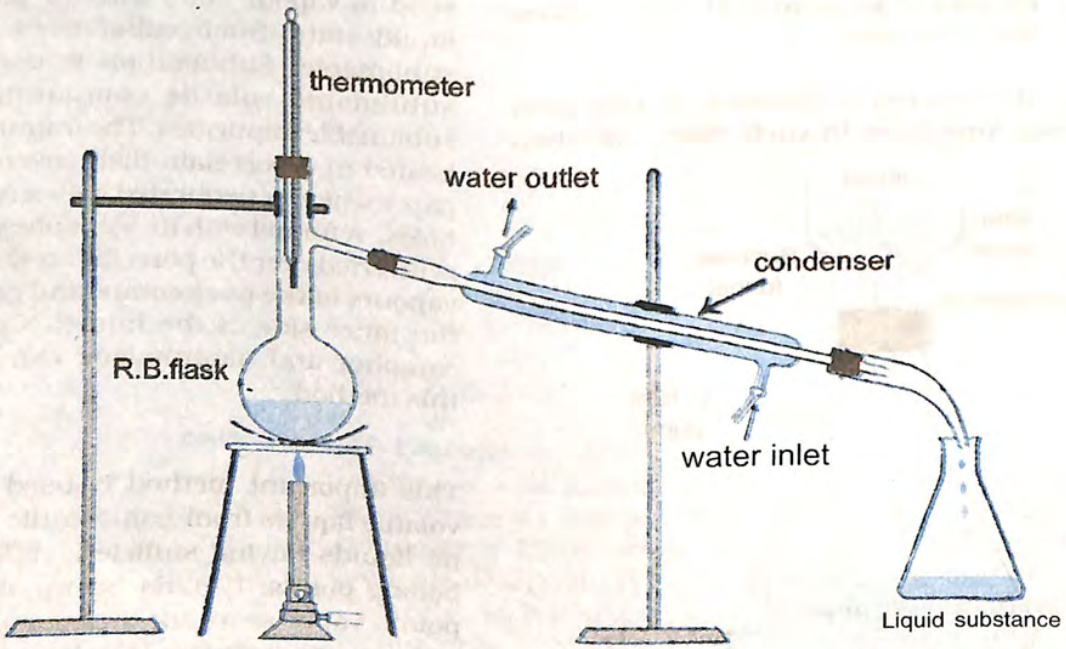


Fig.16.4 *Simple distillation. The vapours of a substance formed are condensed and the liquid is collected in conical flask.*

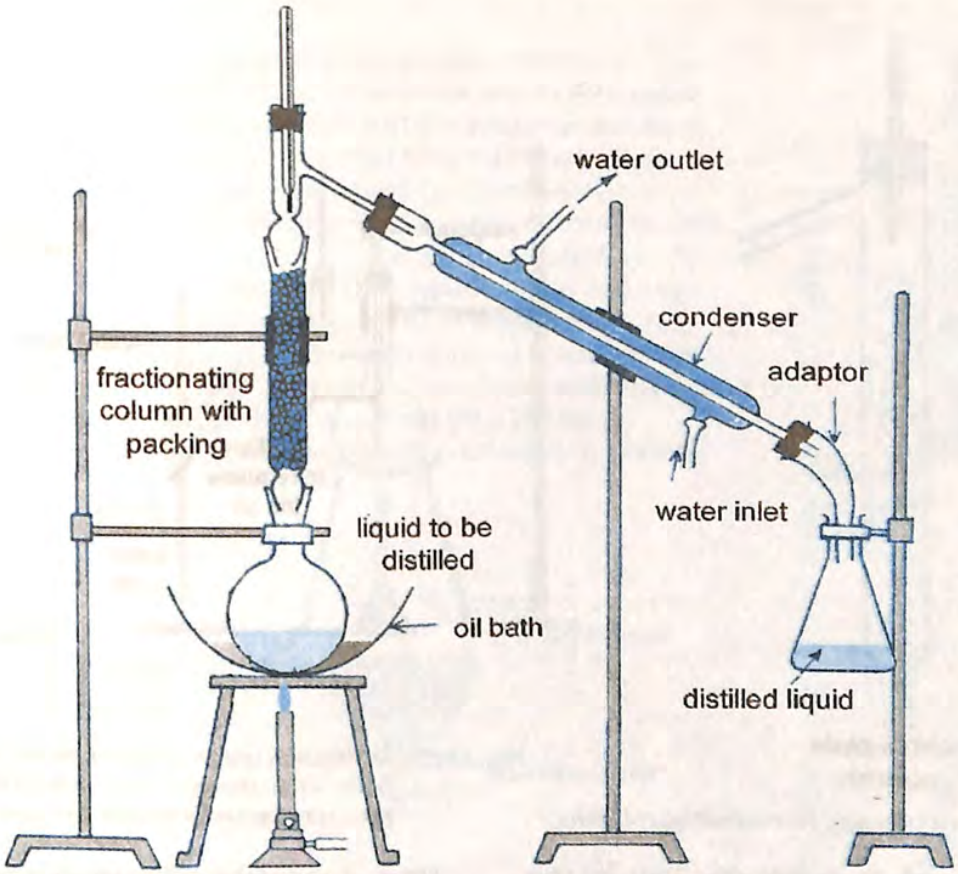


Fig.16.5 *Fractional distillation. The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions.*

column provides many surfaces for heat exchange between the ascending vapours and the descending condensed liquid. Some of the condensing liquid in the fractionating column obtains heat from the ascending vapours and revaporizes. The vapours thus become richer in low boiling component. The vapours of lower boiling component ascend to the top of the column after a series of successive distillations. On reaching the top, the vapours become pure in low boiling component and pass through the condenser and the pure liquid is collected in a receiver. After a series of successive distillations, the remaining liquid in the distillation flask gets enriched in higher boiling component. Each successive condensation and vaporization is called a ***theoretical plate.*** Commercially, columns with hundreds of plates are available.

One of the technological applications of fractional distillation is to separate different fractions of ***crude oil in petroleum industry.***

Distillation Under Reduced Pressure: This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Such liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface. A liquid boils at a temperature at which its vapour pressure is equal to the external pressure. The pressure is reduced with the help of a water pump or vacuum pump (Fig.16.7). Glycerol can be separated from *spent-lye in soap industry* by using this technique.

Steam Distillation: This technique is applied to separate substances which are steam volatile and are immiscible with water. In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound is condensed and collected. The compound is later separated from water using

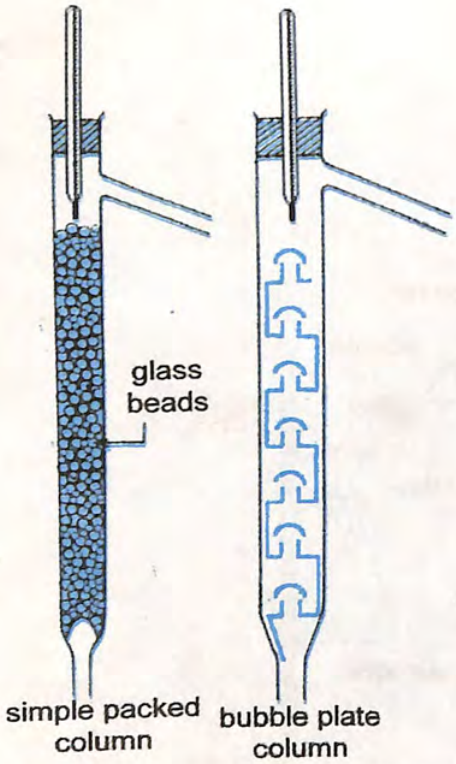


Fig.16.6 *Different types of fractionating columns.*

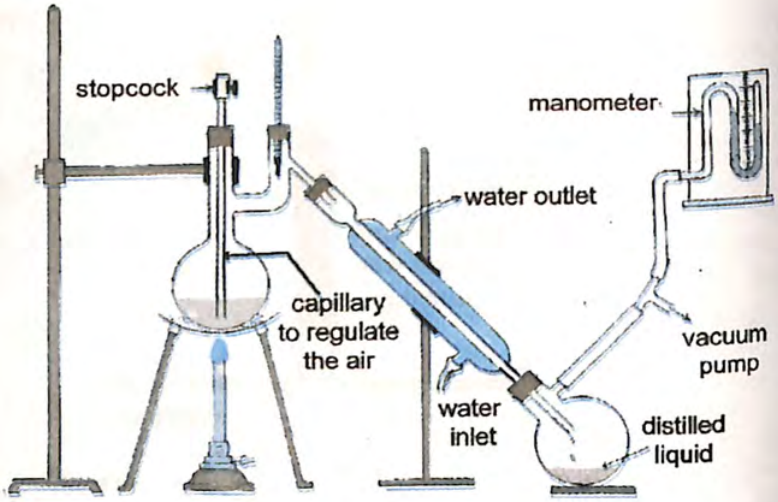


Fig.16.7 *Distillation under reduced pressure. A liquid boils at a temperature below its vapour pressure by reducing the pressure.*

a separating funnel. In steam distillation, the liquid boils when the sum of vapour pressures due to the organic liquid (p_1) and that due to water (p_2) becomes equal to the atmospheric pressure (p), i.e. $p = p_1 + p_2$. Since p_1 is lower than p, the organic liquid vaporizes at lower temperature than its boiling point.

Thus, if one of the substances is water and the other, a water insoluble substance, such a mixture will boil close to but below, 373K. A mixture of water and the substance is obtained which can be separated from aniline-water mixtures using a separating funnel. Aniline is separated by this technique (Fig.16.8).

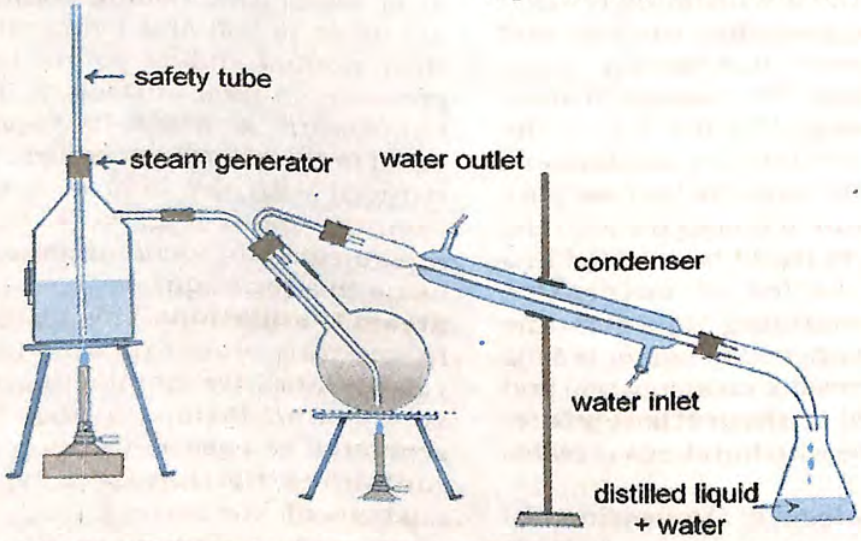


Fig.16.8 *Steam distillation. Steam volatile component volatilizes, the vapours condense in the condenser and the liquid collects in conical flask.*

16.1.5 Differential Extraction

When an organic compound is present in an aqueous medium, it is separated by shaking it with an organic solvent in which it is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they form two distinct layers. The organic solvent is later removed by distillation or by evaporation to get back the compound. Differential extraction is carried out in a separating funnel as shown in figure 16.9(a). If the organic compound is less soluble in the organic solvent, a very large quantity of solvent would be required to extract even a very small quantity of the compound. The technique of ***continuous extraction*** is employed in such cases. The same solvent is repeatedly used for extraction of the compound (Fig.16.9b).

The solid mixture containing the compound is taken in a porous tube 'A' fitted with a thick filter paper. The solvent is taken in flask, B. On heating, vapours of the solvent rise up and condense in the condenser. The condensed solvent reaches in the tube A and extracts the compound. When the level of the liquid in tube A reaches up to the top in tube C, it gets siphoned and is collected in the flask which is being heated continuously. The solvent is distilled and its vapours again reach into the tube A to extract the compound. Thus the process of extraction takes place continuously.

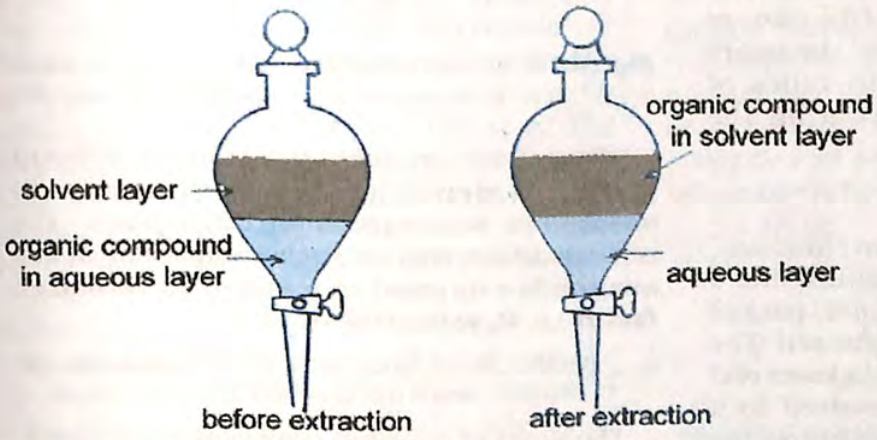


Fig.16.9 *(a) Differential extraction. Extraction of compound takes place based on difference in solubility*

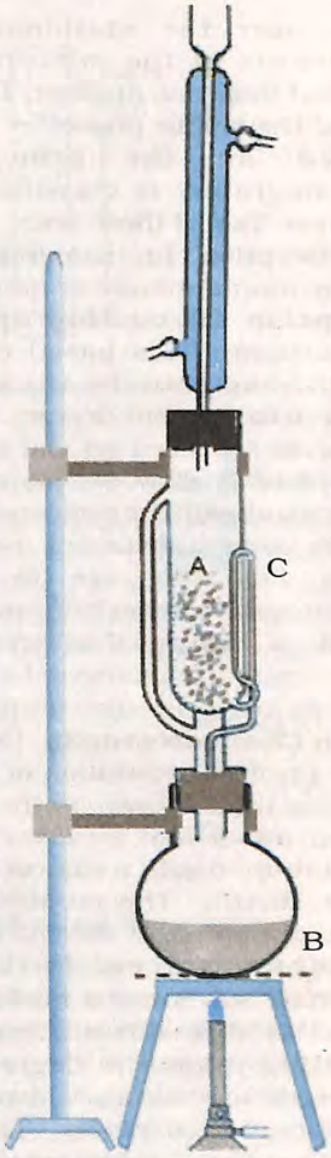


Fig.16.9 *(b) continuous differential extraction of a less soluble component in a solvent.*

16.1.6 Chromatography

Chromatography is an important technique extensively used to separate mixtures into its components, purify compounds and also test the purity of compounds. The name chromatography is based on the greek word chroma, for colour since the method was first used for the separation of coloured substances found in plants. In this technique, the mixture of substances is applied onto a stationary phase, which may be a solid or a liquid. A pure solvent, a mixture of solvents, or a gas is allowed to move

slowly over the stationary phase. The components of the mixture get gradually separated from one another. The moving phase is called the mobile phase.

Based on the principle involved, chromatography is classified into different categories. Two of these are:

(i) Adsorption chromatography and
(ii) Partition chromatography.

***Adsorption Chromatography*:** Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption.

(i) Column chromatography and
(ii) Thin layer chromatography

***Column Chromatography*:** Column chromatography involves separation of a mixture into a long glass tube, known as the column, packed with an adsorbent (stationary phase). The column is fitted with a stopcock at its lower end (Figure 16.10). The mixture dissolved in a minimum amount of solvent is applied on the top of the adsorbent in the column. An appropriate solvent or a mixture of solvents is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, partial or complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column (Fig. 16.10).

***Thin layer Chromatography*:** Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of the substances of a mixture over a thin layer of an adsorbent. A thin layer (about 0.2mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as *thin layer chromatography plate*. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate. The glass plate is then placed in a closed jar containing the solvent (Figure 16.11a) As the solvent jar moves up the plate, the components of the

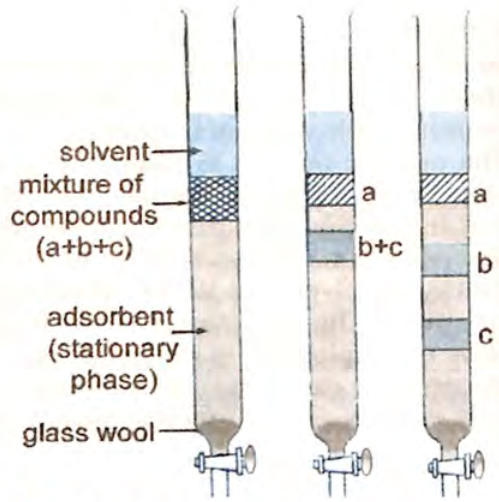


Fig.16.10 *Column chromatography. Different stages of separation of components of a mixture.*

mixture move up along the plate to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its **retention factor** i.e. $\mathbf{R_f}$ **value** (Fig. 16.11 b).

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds which are invisible to the eye but which fluoresce can be detected by putting the plate under ultraviolet light. Another detection technique is to place the plate in a covered jar containing a few crystals of iodine. Spots of compounds, which adsorb iodine, will show up as brown spots. Sometimes an appropriate reagent may also be sprayed on the plate. For example, amino acids may be detected by spraying the plate with ninhydrin solution (Fig. 16.11).

***Partition Chromatography*:** Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase.

A strip of chromatography paper spotted at

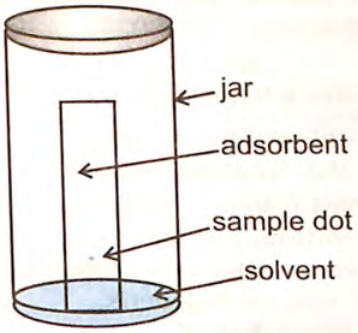


Fig.16.11 (a) Thin layer chromatography. Chromatogram being developed.

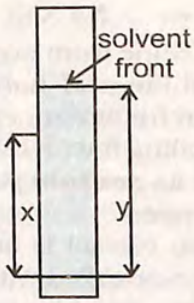


Fig.16.11 (b) Developed chromatogram.

the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents (Figure 16.12). This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the **chromatogram**. The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

16.2 QUALITATIVE ANALYSIS

The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

16.2.1 Detection of Carbon and Hydrogen

Carbon and hydrogen are detected by heating the compound with copper (II) oxide. Carbon present in the compound is oxidized to carbon dioxide (tested with limewater) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

$$C + 2CuO \longrightarrow 2Cu + CO_2$$

$$2H + CuO \longrightarrow Cu + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

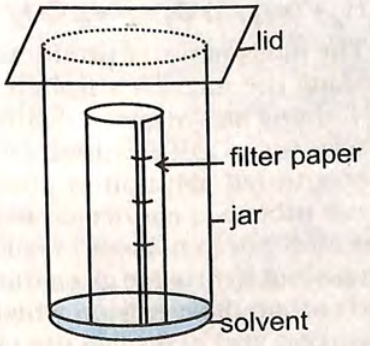
$$4\,H_2O + CuSO_4.\,H_2O \longrightarrow CuSO_4.5H_2O$$

White **Blue**

16.2.2 Detection of other Elements

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by "***Lassaigne's test***". The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. Following reactions take place:

$$Na + C + N \longrightarrow NaCN$$



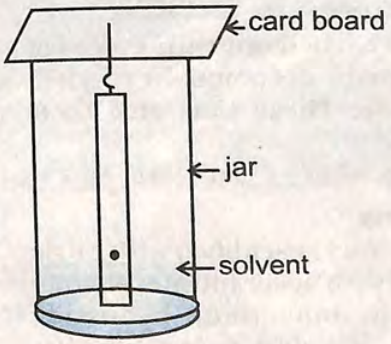


Fig.16.12 Paper chromatography. Chromatography paper in two different shapes.

$2Na + S \longrightarrow Na_2S$

$Na + X \longrightarrow Na\,X$ (X = Cl, Br or I)

C, N, S and X come from organic compound.

Cyanide, sulphide and halide of sodium so formed in sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as ***sodium fusion extract***.

(A) *Test for Nitrogen*

The sodium fusion extract is boiled with iron (II) sulphate and then acidified with sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen. Sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate (II). During heating, some iron (II) ions are oxidised to ferric ions which react with sodium hexacyanoferrate (II) to produce iron (III) hexacyanoferrate (II) (ferriferrocyanide) which is Prussian blue in colour.

$6CN^- + Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}$

$4[Fe(CN)_6]^{4-} + 4Fe^{3+} \longrightarrow Fe_4[Fe(CN)_6]_3$

Prussian blue

(B) *Test for Sulphur*

(a) The *sodium fusion extract* is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$S^{2-} + Pb^{2+} \longrightarrow PbS$

(b) On treating sodium fusion extract with sodium nitroprusside, a violet colour further indicates the presence of sulphur.

$S^{2-} + Fe(CN)_5NO]^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$

Violet

In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no Prussian blue since there are no free cyanide ions.

$Na + C + N + S \longrightarrow NaSCN$

$Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$

If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.

$NaSCN + 2Na \longrightarrow NaCN + Na_2S$

(C) *Tests for Halogens*

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonia shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

$X^- + Ag^+ \longrightarrow AgX$

X represents a halogen – Cl, Br or I.

If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with nitric acid to decompose cyanide or sulphide of sodium formed during *Lassaigne's test*. These ions would otherwise interfere with silver nitrate test for halogens.

(D) *Test for Phosphorus*

The compound is heated with an oxidising agent(sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$

$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow$

Ammonium molybdate

$(NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O$

Ammonium phosphomolybdate

16.3 QUANTITATIVE ANALYSIS

The percentage composition of elements present in an organic compound are determined by the methods based on the following principles:

16.3.1 Carbon and Hydrogen

Both carbon and hydrogen are estimated in one experiment. A known mass of an organic compound is burnt in presence of excess of oxygen and copper (II)oxide. Carbon and hydrogen in the compound are oxidised to carbon dioxide and water respectively.

$C_xH_y + (x+y/4)\,O_2 \longrightarrow x\,CO_2 + y/2\,H_2O$

The mass of water produced is determined by passing the mixture through a weighed U-tube containing anhydrous calcium chloride. Carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide. These tubes are connected in series (Fig. 16.13). The increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

Let the mass of organic compound be *m* g, mass of water and carbon dioxide produced be

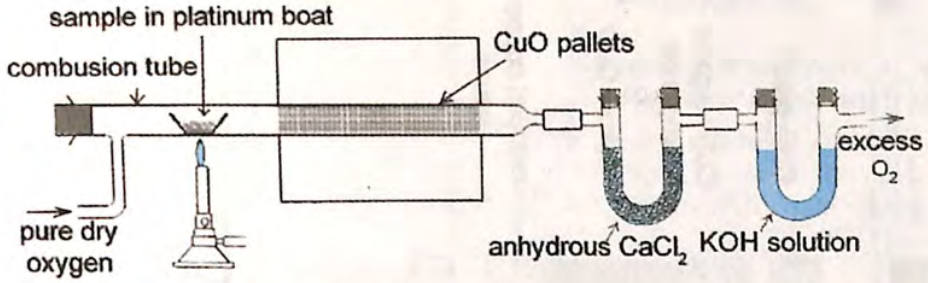


Fig.16.13 *Estimation of carbon and hydrogen. Water and carbon dioxide formed on oxidation of substance are absorbed in anhydrous calcium chloride and potassium hydroxide solutions respectively contained in U tubes.*

m_1 and m_2 g respectively;

$$\text{Percentage of carbon} = \frac{12 \times m_2 \times 100}{44 \times m}$$

$$\text{Percentage of hydrogen} = \frac{2 \times m_1 \times 100}{18 \times m}$$

Example 16.1

On complete combustion, 0.246g of an organic compound gave 0.198g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

Solution

$$\text{Percentage of carbon} = \frac{12 \times 0.198 \times 100}{44 \times 0.246} = 21.95\%$$

$$\text{Percentage of hydrogen} = \frac{2 \times 0.1014 \times 100}{18 \times 0.246} = 4.58\%$$

16.3.2 Nitrogen

There are two methods for estimation of nitrogen: (i) *Dumas method* and (ii) *Kjeldahl's method.*

(i) Dumas method : The nitrogen containing organic compound, when heated with copper oxide in an atmosphere of carbon dioxide, yields free nitrogen in addition to carbon dioxide and water.

$$C_xH_yN_z + (2x+y/2)\,CuO \longrightarrow x\,CO_2 + y/2\,H_2O + z/2\,N_2 + (2x+y/2)\,Cu$$

Traces of nitrogen oxides formed, if any, are reduced to nitrogen by passing the gaseous mixture over a heated copper spiral. The mixture of gases so produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the upper part of the graduated tube (Fig.16.14).

Let the mass of organic compound = m g

Volume of nitrogen collected = V_1 mL

Room temperature = T_1 K

$$\text{Volume of nitrogen at STP} = \frac{P_1V_1 \times 273}{760 \times T_1}$$

(Let it be V mL)

Where P_1 and V_1 are the pressure and volume of nitrogen, P_1 is different from the atmospheric pressure at which nitrogen gas is collected. The value of P_1 is obtained by the relation;

P_1 = Atmospheric pressure – Aqueous tension

22400 mL N_2 at STP weighs 28 g.

$$\text{V mL } N_2 \text{ at STP weighs} = \frac{28 \times V}{22400}\text{ g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times V \times 100}{22400 \times m}$$

Example 16.2

In a Dumas' method for estimation of nitrogen, 0.3g of an organic compound gave 50mL of nitrogen collected at 300K temperature and 715mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K=15mm)

Solution

Volume of nitrogen collected at 300K and 715mm pressure is 50mL

Actual pressure = 715-15 =700mm

$$\text{Volume of nitrogen at STP} = \frac{273 \times 700 \times 50}{300 \times 760} = 41.9\text{ mL}$$

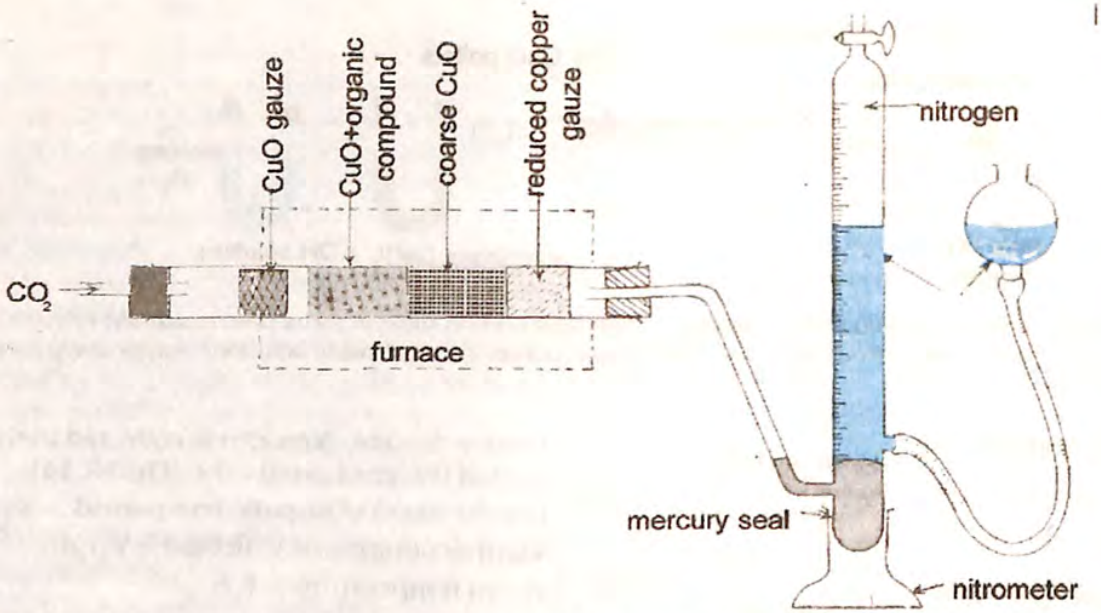


Fig.16.14 *Dumas method. The organic compound yields nitrogen gas on heating it with copper (II) oxide in presence of CO_2 gas, the mixture of gases is collected over potassium hydroxide solution in which CO_2 is absorbed and volume of nitrogen gas is determined.*

22,400 mL of N_2 at STP weighs = 28g

41.9 mL of nitrogen weighs = $\frac{28 \times 41.9}{22400}$ g

Percentage of nitrogen = $\frac{28 \times 41.9 \times 100}{22400 \times 0.3} = 17.46\%$

(ii) Kjeldahl's method: The compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate. The resulting acid mixture is then heated with excess of sodium hydroxide. The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid. The amount of ammonia produced is determined by estimating the amount of sulphuric acid cousumed in the reaction. It is done by estimating unreacted sulphuric acid left after the absorption of ammonia by titrating it with standard alkali solution. The difference between the initial amount of acid taken and that left after the reaction gives the amount of acid reacted with ammonia.

Organic compound + $H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$$\xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

Let the mass of organic compound taken = m g

Volume of H_2SO_4 of molarity, M, taken = V mL

Volume of NaOH of molarity, M, used for titration of excess of $H_2SO_4 = V_1$ mL

V_1 mL of NaOH of molarity M

= $V_1/2$ mL of H_2SO_4 of molarity M

Volume of H_2SO_4 of molarity M unused

= $(V - V_1/2)$ mL

$(V - V_1/2)$ mL of H_2SO_4 of molarity M

= $2(V-V_1/2)$ mL of NH_3 solution of molarity M.

1000 mL of 1 M NH_3 solution contains 17g NH_3 or 14 g N

$2(V-V_1/2)$ mL of NH_3 solution of molarity M contains

$$\frac{14 \times M \times 2(V - V_1/2)}{1000} \text{ g N}$$

$$\text{Percentage of N} = \frac{14 \times M \times 2(V - V_1/2)}{1000} \times \frac{100}{m}$$

$$= \frac{1.4 \times M \times 2(V - V_1/2)}{m}$$

Kjeldahl method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does

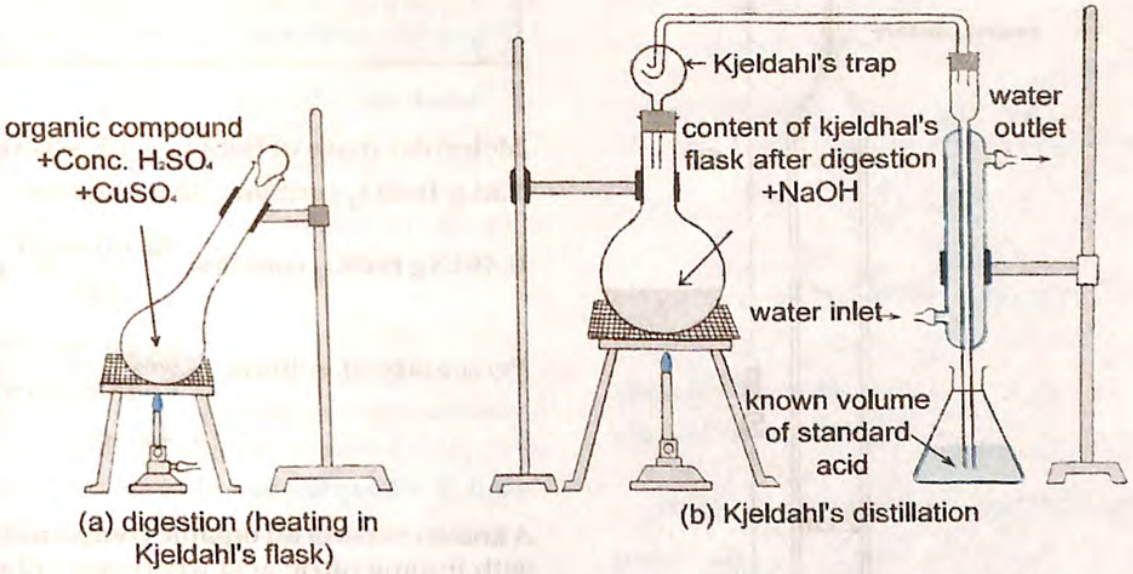


Fig.16.15 Kjeldahl method. Nitrogen-containing compound is treated with concentrated. H_2SO_4 to get ammonium sulphate which liberates ammonia by treating it with NaOH, ammonia is absorbed in known volume of standard acid.

not change to ammonium sulphate under these conditions.

Example 16.3

During nitrogen estimation present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5g of the compound in Kjeldahl's estimation of nitrogen neutralized 10 mL of 1 M H_2SO_4. Find the percentage of nitrogen in the compound.

Solution

1 M of 10 mL H_2SO_4 = 1M of 20 mL NH_3

1000 mL of 1M ammonia contains 14 g nitrogen

20 mL of 1M ammonia contains $\frac{14 \times 20}{1000}$ nitrogen

$$\text{Percentage of nitrogen} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0\%$$

16.3.3 Halogens

Carius method : A known mass of an organic compound is heated, with fuming nitric acid in the presence of silver nitrate containted in a hard glass tube known as Carius tube, (Fig.16.16) in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, dried and weighed.

Let the mass of organic compound taken = m g

Mass of AgX formed = m_1 g

1 mole of AgX contains 1 mole of X

Mass of halogen in m_1g of AgX

$$= \frac{\text{atomic mass of X} \times m_1\text{g}}{\text{molecular mass of AgX}}$$

Percentage of halogen

$$= \frac{\text{atomic mass of X} \times m_1 \times 100}{\text{molecular mass of AgX} \times m}$$

Example 16.4

In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of AgBr. Find the percentage of bromine in the compound.

Solution

Molecular mass of AgBr = 108 + 80 =188 g mol^{-1}

188 g AgBr contains 80 g bromine

0.12 g AgBr contains $\frac{80 \times 0.12}{188}$ g bromine

$$\text{Percentage of bromine} = \frac{80 \times 0.12 \times 100}{188 \times 0.15} = 34.04\%$$

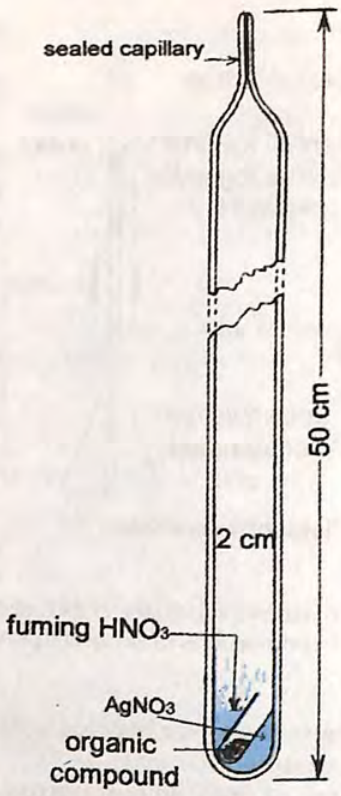


Fig. 16.16 *Carius method. Halogen containing organic compound is heated with fuming nitric acid in presence of silver nitrate.*

16.3.4 Sulphur

A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid. Sulphur present in the compound is oxidized to sulphuric acid. It is precipitated as barium sulphate by adding excess of barium chloride solution. The precipitate is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the mass of barium sulphate.

Let the mass of organic compound taken = m g and the mass of barium sulphate formed = m_1 g

1 mol of $BaSO_4$ = 233 g $BaSO_4$ = 32 g sulphur

m_1 g $BaSO_4$ contains $\frac{32 \times m_1}{233}$ g sulphur

$$\text{Percentage of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m}$$

Example 16.5

In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

Solution

Molecular mass of $BaSO_4$ = 137+32+64 = 233 g

233 g $BaSO_4$ contains 32 g sulphur

0.4813 g $BaSO_4$ contains $\frac{32 \times 0.4813}{233}$ g sulphur

$$\text{Percentage of sulphur} = \frac{32 \times 0.4813 \times 100}{233 \times 0.157}$$

$$= 42.10\%$$

16.3.5 Phosphorus

A known mass of an organic compound is heated with fuming nitric acid whereupon phosphorus present in the compound is oxidized to phosphoric acid. It is precipitated as ammonium phosphomolybdate, $(NH_4)_3\ PO_4.12MoO_3$, by adding ammonia and ammonium molybdate. Alternatively, phosphoric acid may be precipitated as $MgNH_4PO_4$ which on ignition yields $Mg_2P_2O_7$.

Let the mass of organic compound taken = m g and mass of ammonium phospho molydate = m_1 g

Molar mass of $(NH_4)_3\ PO_4\ 12MoO_3$ = 1877 g

$$\text{Percentage of phosphorus} = \frac{31 \times m_1 \times 100}{1877 \times m}\ \%$$

If phosphorus is estimated as $Mg_2P_2O_7$,

$$\text{Percentage of phosphorus} = \frac{62 \times m_1 \times 100}{222 \times m}\ \%$$

Where 222 u is the molar mass of $Mg_2P_2O_7$, m, the mass of organic compound taken, m_1, the mass of $Mg_2P_2O_7$ formed and 62, the mass of two phosphorus atoms present in the compound $Mg_2P_2O_7$.

16.3.6 Oxygen

The percentage of oxygen in an organic compound is usually found by difference between the total percentage composition (100) and the sum of the percentages of all other elements. However, oxygen can also be estimated directly as follows:

A definite mass of an organic compound is decomposed by heating in a stream of nitrogen

gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm iodine pentoxide(I_2O_5) when carbon monoxide is oxidized to carbon dioxide producing iodine.

$$\text{Compound} \xrightarrow{\text{heat}} O_2 + \text{other gaseous products}$$

$$2C + O_2 \xrightarrow{1373K} 2CO$$

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

The percentage of oxygen can be derived from the amount of carbon dioxide or iodine produced.

Let the mass of organic compound taken = m g

Mass of carbon dioxide = m_1 g

44 g carbon dioxide contains 32 g oxygen

m_1 g carbon dioxide contains $\frac{32 \times m_1}{44}$ g oxygen

$$\text{Percentage of oxygen} = \frac{32 \times m_1 \times 100}{44 \times m}$$

Presently the estimation of elements in an organic compound is carried out by using microquantities of substances and automatic experimental techniques. The elements, carbon, hydrogen and nitrogen present in a compound are determined by an apparatus known as **CHN elemental analyzer**. The analyzer requires only a very small amount of the substance (1-3 mg) and displays the values on a screen within a short time. A detailed discussion of such methods is beyond the scope of this book.

16.4 DETERMINATION OF MOLECULAR MASS

The molecular mass of a compound is required for determining its molecular formula. A number of methods are used to determine the molecular mass of a compound depending upon its nature. The methods commonly employed for determining the molecular mass are as follows.

1. Victor Meyer Method.
2. Freezing point depression or boiling point elevation method.
3. Volumetric method.
4. Silver salt method for acids.
5. Chloroplatinate salt method for bases (amines)
6. Mass spectrometry.

We shall discuss here the principles of silver salt and chloroplatinate salt methods and mass spectrometry.

16.4.1 Silver Salt Method

A known mass of an organic acid is converted into its silver salt by using ammoniacal silver nitrate solution. On ignition, the silver salt of the acid leaves a residue of metallic silver.

$$RCOOH \xrightarrow{NH_4OH} RCOONH_4 \xrightarrow{AgNO_3} RCOOAg \xrightarrow{\text{ignite}} Ag$$

Let the mass of carboxylic acid taken = m g

Mass of silver salt formed = m_1 g

Mass of silver residue = m_2 g

$\therefore$ 108 g silver will be obtained from $\frac{m_1 \times 108}{m_2}$ g silver salt.

This is equal to the molar mass of silver salt of a monocarboxylic acid.

Molar mass of RCOOH

= (Molar mass of RCOOAg) – (Atomic mass of Ag) + (Atomic mass of H)

$\therefore$ Molar mass of monocarboxylic acid

$$= \left(\frac{m_1 \times 108}{m_2}\right) - 108 + 1 = \left(\frac{m_1 \times 108}{m_2}\right) - 107$$

In case of polycarboxylic acid of basicity, n : n gram atoms of silver is formed per mole of the acid.

Therefore, the molar mass of silver salt of a polycarboxylic acid of basicity, n :

Molar mass of Polybasic acid

= (Molar mass of silver salt) – (n × atomic mass of silver) + (n × atomic mass of H)

$$= \left[\frac{m_1 \times 108 \times n}{m_2}\right] - 108 \times n + 1 \times n$$

$$= n\left[\left(\frac{m_1 \times 108}{m_2}\right) - 107\right]$$

Example 16.6

A sample of 0.46 g of the silver salt of a dibasic acid gave a residue of 0.324 g of silver on ignition. Determine the molecular mass of the acid.

Solution

Molar mass of silver salt of acid

$$= \frac{0.46 \times 108}{0.324} \times 2 \text{ g mol}^{-1}$$

(where 2 is the basicity of acid)

$$\text{Molar mass of acid} = 2\left(\frac{0.46 \times 108}{0.324} - 107\right)$$

$$= 92.67 \text{ g mol}^{-1}$$

Molecular mass of the acid = 92.67 u

16.4.2 Chloroplatinate Salt Method

Most organic bases, e.g. amines react with chloroplatinic acid (H_2PtCl_6) to form salts, chloroplatinates, of general formula, $B_2H_2PtCl_6$ where B is a monoacidic amine. On heating, these salts decompose and yield metallic platinum.

$$2RNH_2 + H_2PtCl_6 \rightarrow (RNH_3)_2 PtCl_6$$

$$(RNH_2)_2 H_2PtCl_6 \xrightarrow{\text{ignite}} Pt$$

The salt formed with H_2PtCl_6 and diacidic amine, B would be $B_2(H_2PtCl_6)_2$ and with triacidic amine, salt formed would be $B_2(H_2PtCl_6)_3$ and that with amine of acidity n, it would be $B_2(H_2PtCl_6)_n$.

Let the mass of organic compound taken = m g

Mass of chloroplatinate salt taken = m_1 g

Mass of metallic platinum formed = m_2 g

One gram atom of platinum will be obtained from 1 gram mole of chloroplatinate salt.

∴ 195 g (atomic mass of Pt) of Pt is obtained from 1 gram mole of its monoacidic base.

∴ m_2 g platinum will be obtained from m_1 g of platinum salt of monoacidic base.

$$195 \text{ g platinum is obtained from } \frac{m_1 \times 195}{m_2} \text{ g salt}$$

Molar mass of chloroplatinate salt of

(i) monoacidic base $\left[B_2(H_2PtCl_6)\right] = \frac{m_1 \times 195}{m_2}$

(ii) diacidic base $\left[B_2(H_2PtCl_6)_2\right] = \frac{m_1 \times 195}{m_2} \times 2$

(iii) polyacidic base $\left[B_2(H_2PtCl_6)_n\right] = \frac{m_1 \times 195}{m_2} \times n$

Molecular mass of the base, B

= ½ [molar mass of chloroplatinate salt – molar mass of $(H_2PtCl_6)n$]

= ½ [molar mass of chloroplatinate salt – n × (410)]

where 410 is the molar mass of H_2PtCl_6.

Example 16.7

A sample of 0.400 g of the chloroplatinate of a monoacid base on ignition left, 0.125 g of platinum. What is the molecular mass of the base?

Solution

Molar mass of $B_2H_2PtCl_6$ salt

$$= \frac{m_1 \times 195}{m_2} = \frac{0.400 \times 195}{0.125} \text{ g mol}^{-1}$$

$$\text{Molar mass of base } \frac{1}{2}\left[\frac{m_1 \times 195}{m_2} - 410\right]$$

(n=1 since it is a monoacid base)

$$= \frac{1}{2}\left[\frac{0.400 \times 195}{0.125} - 410\right] = 107.00 \text{ g mol}^{-1}$$

Molecular mass of the base = 107 u

16.4.3 Mass spectrometry

The molecular mass of an organic compound is usually determined by an instrument known as **mass spectrometer** (Fig. 16.17). In addition to molecular mass, the mass spectrum of a compound may also reveal information concerning molecular formula and molecular structure of an unknown organic compound. In this technique, a very small amount of a substance is vaporized and bombarded with a beam of very high-energy electrons. The molecules gain energy high enough to emit electrons resulting in the formation of positively charged ions. The ion formed by loss of one electron from the parent molecule is known as **molecular ion**. Majority of ions carry a unit positive charge. The positively charged ions further break into smaller fragments of positive ions due to certain bond cleavages. This resulting mixture of ions is passed between a

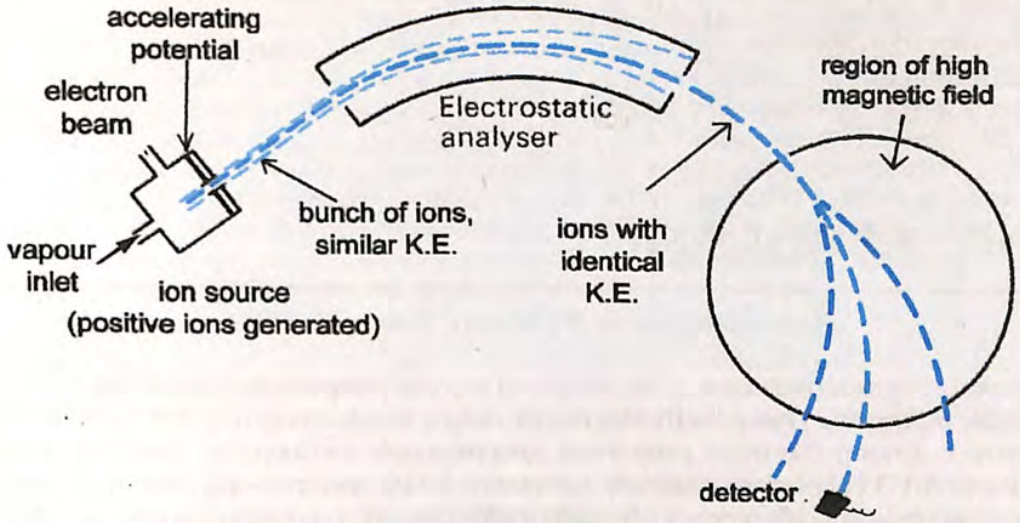


Fig.16.17 *Mass spectrometer. An organic compound is split into small fragments of positive ions, the analyzer separates the fragments according to their mass, the detector measures the relative abundance of ions.*

series of negatively charged metal plates (accelerator), which accelerates them to high speeds. From the accelerator, the ions reach the analyzer where they pass through another electric field. This field makes the particles move in curved paths and directs them into a region of high magnetic field. Here, the ions move in circular paths. The path they take depends on the ratio of their mass and charge (m/z). Finally the ions are brought to the detector, which produces a record of the signals due to all the fragments of the compound, in the form of a graph, known as the **mass spectrum**. The signal produced by the molecular ion is known as the **molecular ion peak**. It gives the molecular mass of the compound.

A common mass spectrometer can resolve mass peaks to the nearest whole number (unit resolution) upto a mass number of about 500. A high-resolution mass spectrometer can resolve peaks differing by as little as 0.001 atomic mass unit.

16.5 DETERMINATION OF EMPIRICAL AND MOLECULAR FORMULAE

The empirical formula of a compound is the simplest formula, which gives the ratio, in whole numbers, in which atoms of different elements are present. It is calculated in two steps; (i) by dividing the percentage compositions of elements by the respective atomic masses and (ii) dividing the numbers so obtained by the lowest number. These numbers are generally whole numbers. If it is not so then, these are converted to whole numbers by multiplying with a suitable common factor.

Molecular formula represents actual number of different atoms present in the molecule. It is related to empirical formula by the relation.

$$\text{Molecular formula} = (\text{Empirical formula})_n$$

$$\text{where } n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

Following example would illustrate this.

Example 16.8

An organic compound contains C= 61.00%, H = 11.88% and O = 27.12%. Calculate the empirical and molecular formulae of the compound. Molecular mass of the compound is 118.

Calculation of Empirical formula

Element	Percentage composition	Relative no. of atoms	Simplest ratio
Carbon	61.00	$\frac{61.00}{12} = 5.08$	$\frac{5.08}{1.70} = 2.99 = 3$
Hydrogen	11.88	$\frac{11.88}{1} = 11.8$	$\frac{11.88}{1.70} = 6.9 = 7$
Oxygen	27.12	$\frac{27.12}{16} = 1.70$	$\frac{1.70}{1.70} = 1$

Empirical formula = C_3H_7O

Calculation of molecular formula

Empirical formula mass

$= 12 \times 3 + 1 \times 7 + 16 \times 1 = 59$

$$n = \frac{118}{59} = 2$$

Molecular formula = $(C_3H_7O)_2 = C_6H_{14}O_2$

Spectroscopy in Structure Determination

Modern techniques of determination of structures of organic compounds extensively involve the use of spectroscopic methods. These methods require only a small amount of the substance and take much less time. Among the most prominent spectroscopic techniques used are infrared (IR), ultraviolet-visible (UV-Vis.) nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry. The molecule absorbs a specific amount of energy in discrete units corresponding to specific frequency or wavelength of radiation. The energy absorbed by the molecule may cause electronic transition (UV-Vis.), vibrational and rotational energy change (IR,Raman), nuclear magnetic transition (NMR) or ionization and fragmentation of molecules,(mass spectrometry).

The radiation causing electronic absorptions are in ultraviolet and visible region (UV region : 200-400 nm and visible region is 400-800 nm), vibrational in the infrared (4000-650 cm^{-1}) and rotational in the far infrared and microwave regions. The characteristic structural features like presence of double bond, triple bond, conjugation, carbonyl, hydroxyl groups etc. are easily detected by UV-Vis, and IR spectroscopic methods.

Nuclear Magnetic Resonance (NMR) involves magnetic excitation of nuclei of certain atoms like ^1_1H, $^{13}_6C$ *etc. Proton* $\left(^1_1H\right)$ *NMR spectrum shows hydrogen atoms bonded to different atoms and in different electronic environments. For example, the protons of* $CH_3 - Cl$ *and* $H_2C = C<$ *are indicated by different signals in NMR spectrum. Thus different types of spectroscopic analyses combined with physical data and chemical characteristics enable an organic chemist to derive the structure of a given compound. Some other useful structural elucidation techniques are emission, fluorescence, phosphorescence spectroscopy . The three dimensional structure of an organic compound can be determined by x-ray diffraction technique.*

SUMMARY

Purification, qualitative and quantitative analysis and molecular mass determination of organic compounds are carried out for determining their structures. The methods of purification, namely filtration, distillation, sublimation and differential extraction are based on the difference in one or more physical properties, namely solubility, boiling point and vapour pressure of compounds. *Chromatography* is a useful technique of separation and purification of compounds. Based on the principle involved, chromatography is classified into two categories; adsorption and partition chromatography. Adsorption chromatography is based on differential adsorption of various components of a mixture on an adsorbent. Partition chromatography involves continuous partitioning of the components of a mixture between stationary and mobile phases. After getting the compound in pure form, its qualitative analysis is carried out for detection of elements present in it. Carbon and hydrogen are detected by converting them to carbon dioxide and water respectively. Nitrogen,

sulphur, halogens and phosphorus are detected by *Lassaigne's test.* Carbon and hydrogen are estimated by determining the amounts of carbon dioxide and water produced on their oxidation with copper (II) oxide. Nitrogen is estimated by Dumas or Kjeldahl method, and halogens by Carius method. Sulphur and phosphorus are estimated by oxidizing them to sulphuric and phosphoric acids respectively. The percentage of oxygen is usually determined by difference between the total percentage (100) and the sum percentage of all other elements. Direct estimation of oxygen of a compound involves the use of iodine pentoxide.

The molecular mass of a compound may be determined by any one of a number of physico-chemical methods. Silver salt and chloroplatinate salt methods are used to determine the molecular masses of acids and bases respectively. Mass spectrometry is a useful technique of determining the molecular masses of compounds.

EXERCISES

16.1 Give a brief description of the principles of the following processes taking an example in each case;
(i) Filtration, (ii) Recrystallization, (iii) Distillation, and (iv) Chromatography.

16.2 Explain the principle of steam distillation.

16.3 What is the difference between distillation, distillation under reduced pressure and steam distillation?

16.4 Describe the method, which can be used to separate two compounds with different solubilities in a solvent X.

16.5 Discuss the chemistry of Lassaigne's test.

16.6 A mixture contains two components A and B. The solubilities of A and B in water near its boiling point are 10 grams per 100 mL and 2g per 100 mL respectively. How will you separate A and B from this mixture?

16.7 Outline the principle of estimation of nitrogen in an organic compound by (i) Dumas' method and (ii) Kjeldahl's method.

16.8 Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.

16.9 Explain the steps involved to determine empirical formula of an organic compound.

16.10 Define (i) empirical formula and (ii) molecular formula. What is the relation between the two formulae?

16.11 Explain the principle of paper chromatography.

16.12 Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

16.13 Why is an organic compound fused with sodium for testing nitrogen, sulphur and phosphorus?

16.14 Write the molecular formula of Iron (III) haxacyanoferrate (II)

16.15 What is the basic function of mass spectrometry? What is its principle?

16.16 A mixture contains Benzoic acid and nitrobenzene. How can this mixture be separated into its constituents by the technique of extraction using an appropriate chemical reagent?

16.17 A mixture contains 71 per cent of calcium sulphate and 29 per cent of camphor. Name a suitable technique of separation of the components of this mixture.

16.18 Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

16.19 The R_f values of A and B in a mixture determined by TLC in a solvent mixture are 0.65 and 0.42 respectively. If the mixture is separated by column chromatography using the same solvent mixture as a mobile phase, which of the two components, A or B, will elute first? Explain.

16.20 Suggest a suitable technique of separating naphthalene from kerosene present in a mixture.

16.21 Explain why an organic liquid vaporizes at a temperature below its boiling point in its steam distillation?

16.22 Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

16.23 Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

16.24 An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20g of this substance is subjected to complete combustion.

16.25 A sample of 0.50g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5M H_2SO_4. The residual acid required 60 mL of 0.5M solution of NaOH for neutralization. Find the percentage composition of nitrogen in the compound.

16.26 On analysis, 0.2 g of a monobasic acid gave 0.505 g of CO_2 and 0.0864 g of H_2O. 0.305 g of this acid required 25 mL of M/10 NaOH solution for neutralization. Find the molecular formula of the acid.

16.27 A liquid aromatic organic compound A containing carbon=92.3% and hydrogen=7.7% decolourised $KMnO_4$ and on ozonlysis gave methanal and another compound, B. The molecular mass of A is 104. On treatment with a suitable catalyst, A gave a high molecular mass solid product C having the same empirical formula as that of compound A. Compound C is used in making toys and household goods. Identify A, B and C and explain the reactions.

16.28 A sample of 0.246g of an organic compound gave 0.198 g of CO_2 and 0.1014 g of H_2O on complete combution. 0.37 g of the compound gave 0.638g of silver bromide in Carius method. What is the molecular formula of the compound if its molecular mass is 109.

UNIT 17

ORGANIC COMPOUNDS WITH FUNCTIONAL GROUPS CONTAINING HALOGENS

(Haloalkanes and Haloarenes)

Objectives

After studying this Unit, you will be able to

- classify and name organic halogen compounds.
- learn the methods of preparation of organic halogen compounds.
- correlate the physical properties of organic halogen compounds with their structure.
- know the important reactions of organic halogen compounds.
- understand the mechanisms of nucleophilic substitution reactions.
- appreciate the chemistry of some important halogen compounds and their uses.

In Unit 15, you have learnt that hydrocarbons react with halogens and hydrogen halides to give compounds containing one or more halogen atoms. In these compounds, the halogen atom is the functional group, bonded to a carbon atom with a covalent bond. Since these compounds are derived from hydrocarbons, they are known as halogen derivatives of hydrocarbons. Many halogen containing organic compounds occur in nature and some of these are clinically useful. For example, the chlorine-containing antibiotic chloromycetin (chloroamphenicol) produced by a soil microorganism, is very effective for the treatment of typhoid fever. Our body produces an iodine-containing hormone known as thyroxine, the deficiency of which causes a condition called goiter. Some synthetic organic halogen compounds are also important in health care and medicine. For example, chloroquine is used for the treatement of malaria and halothane ($CF_3CHClBr$) is an anaesthetic used during surgery. Certain fully fluorinated compounds are being considered as potential blood substitutes in surgery. Synthetic organic halogen compounds are of great importance in agriculture and industry, and are manufactured in large quantities every year. Organic halogen compounds serve as important intermediates for the synthesis of a wide range of other substances. In this unit you will study the preparation, properties and uses of simple organic halogen compounds.

17.1 CLASSIFICATION

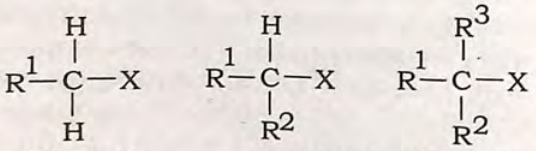
The halogen derivatives of hydrocarbons may be classified as fluoro, chloro, bromo or iodo compounds according to the type of halogen present, and as mono, di, tri,..... halo compounds depending on whether they contain one, two,

three,..... halogen atoms in their molecular structure. Monohalo compounds may further be classified according to the hybridization of the carbon atom bonded to the halogen as discussed below. This classification is useful because it organises them into groups whose members display similar chemical properties.

17.1.1 Compounds containing C_{sp^3}-X bond (X=F,Cl,Br,I):

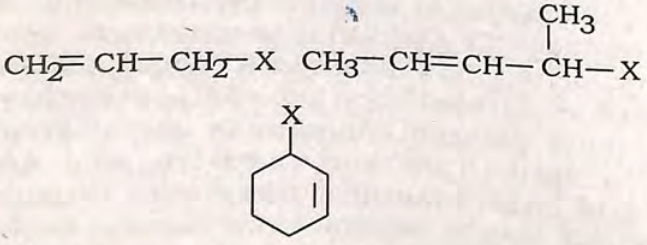
This class includes:

(A) Haloalkanes or Alkyl halides (R-X): In alkyl halides, the halogen atom (X) is bonded to an alkyl group(R). They form a homologous series represented by $C_nH_{2n+1}X$. They are further classified as primary, secondary or tertiary halides according to whether the halogen atom is linked to a primary, secondary or tertiary carbon atom.

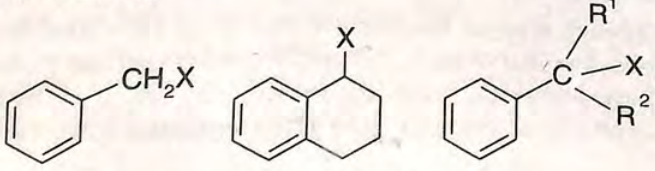


If R is alicyclic in R-X, the halide is a cycloalkyl halide or halocycloalkane, which may be secondary or tertiary.

(B) Allylic halides: In these halides, the halogen is bonded to an sp^3-hybridised carbon atom next to a carbon-carbon double bond, i.e. to an allylic carbon. Some examples are:



(C) Benzylic halides: In these halides, the halogen is bonded to an sp^3-hybridised carbon atom next to an aromatic ring, i.e. to a benzylic carbon, e.g.

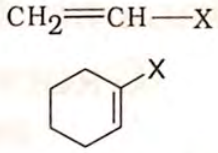


Benzylic and allylic halides may be primary, secondary, or tertiary.

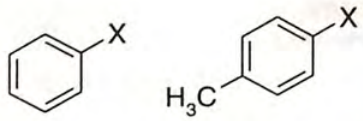
17.1.2 Compounds containing C_{sp^2}-X or C_{sp}-X bond

This class of compounds includes:

(A) Vinylic halides: These halides have the halogen bonded to one of the carbon atoms of a carbon-carbon double bond, i.e. to a vinylic carbon, e.g.,



(B) Aryl halides: The halogen atom in these halides is directly linked to an aromatic ring carbon, e.g.,

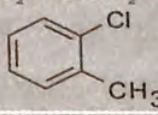
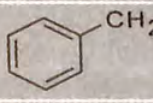


Aromatic halogen compounds are called haloarenes. Thus, benzylic and aryl halides are special types of haloarenes.

17.2 NOMENCLATURE

As you have already learnt in Unit 14, halogen derivatives of hydrocarbons are named as halosubstituted hydrocarbons in the IUPAC system of nomenclature. The common names of alkyl halides are derived by naming the alkyl group followed by the halide. The dihaloalkanes having the same type of halogen atoms are named as alkylidene or alkylene dihalides (or simply halides) depending upon whether the halogen atoms are present at the same (*gem*) or adjacent (*vic*) carbon atoms, respectively. Trihalomethanes and tetrahalomethanes are named as haloforms and carbon tetrahalides, respectively. Fully halogenated hydrocarbons are also called perhalohydrocarbons (per=thoroughly). Compounds having several halogen atoms (polyhaloalkanes) and other more complex halogen compounds are generally named according to IUPAC system. The IUPAC and common names of some halogen compounds are given in Table 17.1.

Table 17.1 IUPAC and Common Names of Some Organic Halogen Compounds

Structure	IUPAC name	Common name
$CH_3CH_2CH(Cl)CH_3$	2-Chlorobutane	*Sec*-Butyl chloride
$(CH_3)_3CCH_2Br$	1-Bromo-2,2-dimethylpropane	*neo*-Pentyl bromide
$CH_2=CH-Cl$	Chloroethene	Vinyl chloride
$CH_2=CHCH_2Br$	3-Bromopropene	Allyl bromide
	1-Chloro-2-methylbenzene	*o*-Chlorotoluene
	1-Chloro-phenylmethane or Chloromethylbenzene	Benzyl chloride
CH_2Cl_2	Dichloromethane	Methylene chloride
$CHBr_3$	Tribromomethane	Bromoform
CCl_4	Tetrachloromethane	Carbon tetrachloride
$ClCH_2CH_2Cl$	1,2-Dichloroethane	Ethylene chloride
$CH_3CH_2Cl_2$	1,1-Dichloroethane	Ethylidene chloride
$CF_3CF_2CF_3$	Octafluoropropane	Perfluoropropane

Example 17.1

Draw the structures of all eight structural isomers that have the molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

Solution

$CH_3CH_2CH_2CH_2CH_2Br$	1-Bromopentane primary
$CH_3CH_2CH_2CH(Br)CH_3$	2-Bromopentane secondary
$CH_3CH_2CH(Br)CH_2CH_3$	3-Bromopentane secondary
$(CH_3)_2CHCH_2CH_2Br$	1-Bromo-3-methylbutane primary
$(CH_3)_2CHCH(Br)CH_3$	2-Bromo-3-methylbutane secondary
$(CH_3)_2C(Br)CH_2CH_3$	2-Bromo-2-methylbutane tertiary
$CH_3CH_2CH(CH_3)CH_2Br$	1-Bromo-2-methylbutane primary
$(CH_3)_3CCH_2Br$	1-Bromo-2,2-dimethylpropane primary

17.3 NATURE OF THE C-X BOND

As described earlier (Units 6,14), the C-X bond is a covalent bond with partial polar character. The C-X bond length increases and bond energy decreases as we move down the group in the periodic table from fluorine to iodine. Some typical bond lengths, bond energies, and dipole moments are given in Table 17.2.

17.4 PHYSICAL PROPERTIES

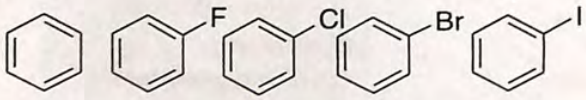
Alkyl halides are colourless when pure, but bromides and particularly iodides develop colour when exposed to light. Methyl chloride, methyl bromide, ethyl chloride and some chlorofluromethanes and chlorofluoroethanes are gases at ambient temperatures. Other chloro, bromo, iodo compounds are liquids or solids. Many volatile halogen compounds have sweet smell. The molecules of organic halogen compounds are generally polar due to the presence of polar C-X bond. Due to the greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives. Consequently, the boiling points of chlorides, bromides and iodides are considerably higher than those of the corresponding hydrocarbons. For monohalogen compounds, the boiling point increases with increasing molecular mass.

Table 17.2 Some Physical Data of Halomethanes(CH_3-X)

Halomethane	C-X bond length/pm	C-X bond energy/ kJmol^{-1}	Dipole moment/Cm
CH_3F	139	452	6.17×10^{-30}
CH_3Cl	178	351	6.24×10^{-30}
CH_3Br	193	293	6.04×10^{-30}
CH_3I	214	234	5.40×10^{-30}

With a fixed hydrocarbon group, it follows the order: fluoride< chloride < bromide < iodide.

	CH_4	CH_3F	CH_3Cl	CH_3Br	CH_3I
b.p./K	111	195	249	277	315



b.p./K 353 358 405 429 462

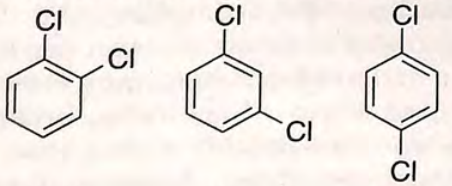
With a given halogen, the boiling point increases with increasing size and decreases with increasing branching of the hydrocarbon part. For example:

	CH_3Cl	CH_3CH_2Cl	$CH_3CH_2CH_2Cl$	$CH_3CH_2CH_2CH_2Cl$	$CH_3CH(CH_3)CH_2Cl$
b.p./K	249	285.5	320	351.5	342
	$CH_3CH_2CH(Cl)CH_3$		$(CH_3)_3C$-Cl		
b.p./K	341		324		

Generally, the boiling points of chloro, bromo and iodo compounds increase as the number of halogen atoms increases. For example:

	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
b.p./K	249	313	334	350

The boiling points of isomeric dihalobenzenes are very nearly the same but the melting points of the *para* isomers are considerably higher than the *ortho* and *meta* isomers. Being more symmetrical, the *para* isomer fits better in the crystal lattice of the solid form than the *ortho* or *meta* isomer.



b.p./K	453	446	448
m.p./K	256	249	323

Simple monofluroro and monochloro compounds are lighter than water but the monobromo and monoiodo compounds are heavier. The density increases with increasing number and atomic mass of the halogen.

	CH_2Cl_2	$CHCl_3$	CCl_4
Density (g/mL)	1.336	1.489	1.595

All the halogen derivatives of hydrocarbons are insoluble in water because they are unable to form hydrogen bond with water or to break the hydrogen bond already present in water. Chloro, bromo and iodo derivatives are soluble in organic solvents such as benzene, ether etc., as intermolecular forces in these derivatives are similar to that in these solvents.

Organic halogen compounds are less inflammable than the hydrocarbons. The inflammability decreases with increasing halogen content. Because they are good solvents for fats and oils and they do not catch fire easily, polychloro compounds, such as tri- and tetra-chloroethylenes are widely used as solvents for dry cleaning, and carbon tetrachloride is used in fire extinguishers.

Example17.2

Arrange each set of compounds in order of increasing boiling point. (a) Bromomethane, bromoform, chloromethane, dibromomethene (b) propane, 1-chloropropane, isopropyl chloride, 1-chlorobutane.

Solution

(a) Chloromethane, bromomethane, dibromomethane, bromoform. Boiling point increases with increasing molecular mass.

(b) Propane, isopropyl chloride, *1*-chloropropane. 1-chlorobutane, Isopropyl chloride being branched has lower b.p. than 1-chloropropane.

17.5 METHODS OF PREPARATION

17.5.1 From hydrocarbons

(A) By free radical halogenation: Free radical chlorination or bromination of alkanes usually gives a complex mixture of isomeric mono- and poly-haloalkanes which is difficult to separate into pure compounds. Furthermore, the yield of any one compound is low due to the formation of other chloro and bromo compounds (Unit 15). For example:

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2 \,/\, \text{UV light}} \underset{+}{CH_3CH_2CH_2CH_2Cl} \\ CH_3CH_2CH(Cl)CH_3$$

isomeric monochloro compounds

$$\left[\begin{array}{ll} + \; CH_3CH(Cl)CH(Cl)CH_3 & + \; CH_3CH_2CH(Cl)CH_2Cl \\ + \; CH_3CH(Cl)CH_2CH_2Cl & + \; CH_3CH_2CH_2CHCl_2 \\ + \; CH_3CH_2CCl_2CH_3 & + \; ClCH_2CH_2CH_2CH_2Cl \end{array}\right] + \text{etc.}$$

isomeric dichloro compounds

Therefore, halogenation of alkanes is not suitable for the laboratory preparation of pure haloalkanes. However, free radical substitution is still useful in certain cases, e.g.,

(i) when the formation of isomeric products is not possible and the mixture can be separated easily due to suitable difference in the boiling points of different products, e.g.,

$$CH_4 + Cl_2 \xrightarrow[\text{or heat}]{\text{UV light}} CH_3Cl + CH_2Cl_2 + CHCl_3 \\ + CCl_4 + HCl$$

$$H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3 + Cl_2 \xrightarrow[\text{or heat}]{\text{UV light}} H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2Cl + HCl$$

Neopentane — Neopentyl chloride

(ii) when the difference in the reactivity of hydrogens attached to different types of carbon atoms is large so that only one product is formed under suitable conditions. The reactivity of different types of hydrogens follows the order:

benzylic ≈ allylic > tertiary > secondary > primary > vinylic ≈ aryl

which is opposite to the C-H homolytic bond dissociation energies. In fact, the vinylic and aryl hydrogens are so unreactive that they do not participate in free radical halogenations. Thus, allylic and benzylic halides can be prepared from alkenes and arenes without much complication, e.g.,

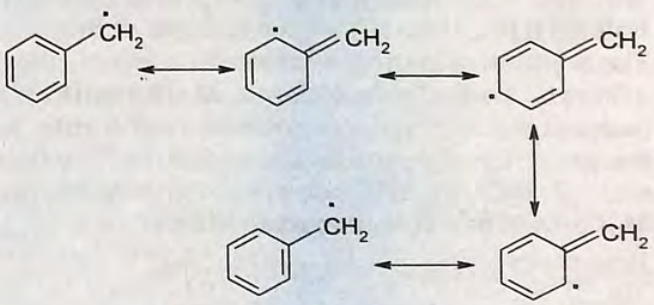
$$CH_2{=}CH-CH_3 + Cl_2 \xrightarrow[\text{gas phase}]{773-873K} CH_2{=}CH-CH_2Cl \\ + HCl$$

$$\underset{\text{Toluene}}{\text{C}_6\text{H}_5CH_3} + Br_2 \xrightarrow[\text{reflux}]{\text{light}} \underset{\text{Benzyl bromide}}{\text{C}_6\text{H}_5CH_2Br} + HBr$$

The high reactivity of allylic and benzylic hydrogen atoms can be explained in terms of stabilization by resonance of the allylic and benzylic free radical intermediates formed during the reaction.

$$CH_2{=}CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH{=}CH_2$$

resonance in allyl radical



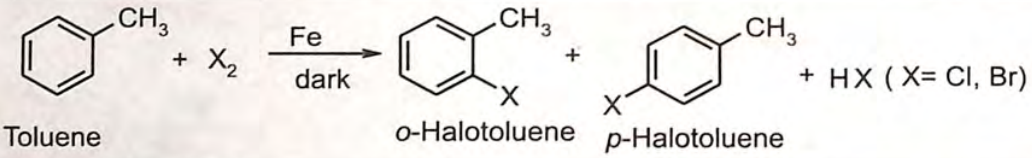
resonance in benzyl radical

(iii) when pure products are not required, such as those used as industrial solvents. Thus, free radical halogenation is an important reaction in industry. If required, the product mixture can be separated into useful fractions by fractional distillation. Moreover, by adjusting the proportion of the reactants, one of the products can be made to predominate, which can be separated in acceptable yield and purity. For instance, methyl

chloride can be obtained as the major product by taking large excess of methane. The unreacted methane can then be separated and recycled. All the chloro and bromo derivatives of methane are obtained industrially by this method.

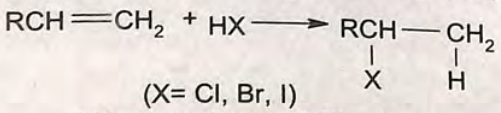
Fluorination with fluorine is highly exothermic and violent. It leads to polysubstitution and cleavage of carbon-carbon bonds. Iodine is too unreactive to bring about free radical iodination.

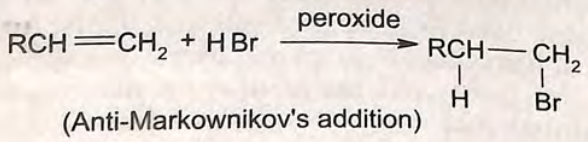
(B) By electrophilic substitution: As discussed in Unit 15, aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively, in the presence of iron, iron(III) halide or other Lewis acid catalysts. For example:

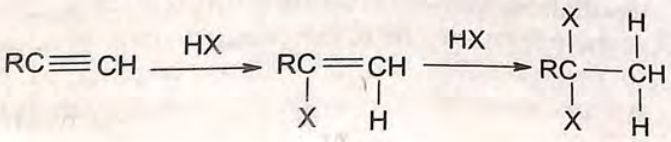


The *ortho* and *para* isomers can easily be separated due to large difference in their melting points. Reaction with iodine is reversible in nature and requires the presence of an oxidising agent (HNO_3, HIO_3) to oxidise the HI formed during iodination. Fluro compounds are not prepared by this method due to high reactivity of fluorine.

(C) By electrophilic addition: As discussed in Unit 15, alkenes and alkynes undergo electrophilic addition with halogens (Cl_2,Br_2) and hydrogen halides (HCl, HBr, HI) to give halogen derivatives. The addition of hydrogen halides to unsymmetrical alkenes and alkynes obeys **Markownikov's** (sometimes also spelt as Makownikoff's) **rule**. In the presence of peroxides the addition of HBr (but not of HCl or HI) occurs contrary to the Markownikov's rule (**peroxide effect**).







17.5.2 From alcohol

In laboratory, alkyl halides are best prepared from alcohols, which are easily accessible. The hydroxy group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride. Phosphorus tribromide and triiodide are generally generated *in situ* (produced in the reaction mixture) by the reaction of red phosphorus with bromine and iodine, respectively. The reaction with halogen acid is catalysed by an acid such as $ZnCl_2$ or H_2SO_4. Hydrobromic acid may be generated *in situ* by the reaction of NaBr or KBr with conc. H_2SO_4.

The reactivity of alcohols follows the order: primary < secondary < tertiary.

For example:

$$ROH + HX \rightarrow RX + H_2O \quad (X=Cl, Br, I)$$

$$ROH + NaBr + H_2SO_4 \rightarrow RBr + NaHSO_4 + H_2O$$

$$3ROH + PX_3 \rightarrow 3RX + H_3PO_3 \ (X=Cl, Br)$$

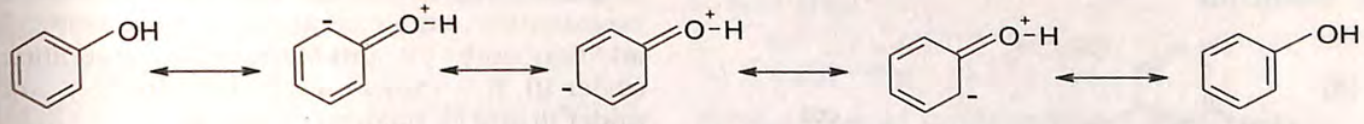
$$ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$$

$$ROH \xrightarrow[(X_2=Br_2,I_2)]{\text{red } P/X_2} RX$$

$$ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$$

Thionyl chloride is preferred for the preparation of chloro compounds because both the by products (SO_2 and HCl) are gaseous which escape from the reaction mixture. This makes the purification of the chloro compounds easy.

The above methods are not applicable for the preparation of aryl halides because it is difficult to replace the hydroxy group of phenols by a halo group. Due to resonance, the carbon-oxygen bond in phenols has partial double bond character, and is, therefore, stronger than the carbon-oxygen single bond in alcohols. Consequently, the cleavage of the carbon-oxygen bond in phenols is difficult.



resonance in phenol

17.5.3 From alkyl chlorides and bromides: Halogen exchange as a way to alkyl iodides and fluorides

Alkyl iodide is often prepared from the corresponding chloride or bromide by treatment with a solution of sodium iodide in acetone. The chlorine or bromine atom of the alkyl halide is replaced by iodine atom in this reaction (**Finkelstein reaction**).

$$R-X+NaI \xrightarrow[\text{reflux}]{\text{acetone}} R-I+NaX\ (X=Cl, Br)$$

Sodium chloride and sodium bromide are less soluble in acetone than sodium iodide. Therefore, they precipitate from the solution, thus preventing the backward reaction to occur. The reaction gives the best results with primary halides.

The best way to prepare alkyl fluorides is by halogen exchange. An alkyl chloride or bromide is heated in the presence of a metallic fluoride, such as AgF, Hg_2F_2, CoF_3 or SbF_3 to give alkyl fluoride(**Swarts reaction**).

$$CH_3Br + AgF \rightarrow CH_3F + AgBr$$

When the organic halide contains two or three halogen atoms at the same carbon, CoF_3 or the more easily accessible SbF_3 is used. For example:

$$3CH_3CCl_2CH_3 + 2SbF_3 \rightarrow 3CH_3CF_2CH_3 + 2SbCl_3$$

The introduction of fluorine and iodine into an aromatic ring requires special methods, which you will study in the higher classes.

Example 17.3

Identify all the possible monochloro structural isomers that would be expected to form on free radical chlorination of $(CH_3)_2CHCH_2CH_3$.

Solution

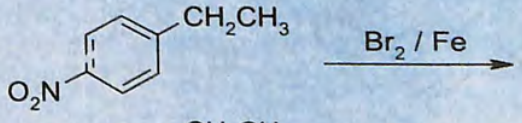
In the given molecule, there are four different types of hydrogen atoms. Replacement of these hydrogen atoms will give the following four monochloro derivatives:

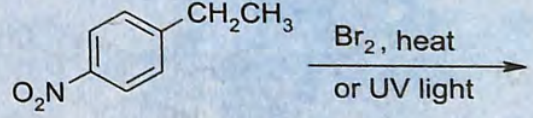
$(CH_3)_2CHCH_2CH_2Cl$ $(CH_3)_2CHCH(Cl)CH_3$

$(CH_3)_2C(Cl)CH_2CH_3$ $CH_3(CH_2Cl)CHCH_2CH_3$

Example 17.4

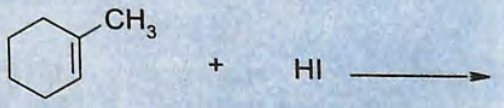
Draw the structure of the major monohalo product in each of the following reactions:

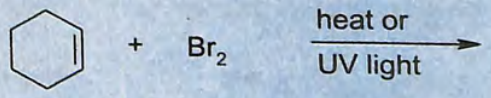
(a) 

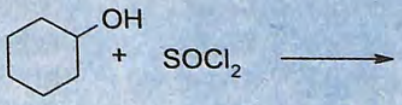
(b) 

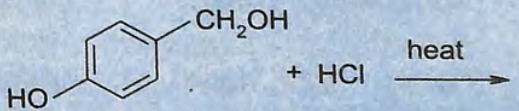
(c) $CH_3CH_2C\equiv CH + HCl$ (1 equiv.) $\longrightarrow$

(d) $CH_3CH_2C(CH_3)=CH_2 + HBr \xrightarrow{\text{peroxide}}$

(e) 

(f) 

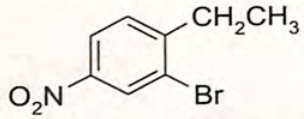
(g) 

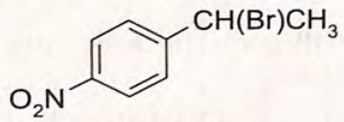
(h) 

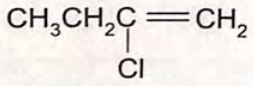
(i) $CH_3CH_2Br + NaI \xrightarrow[\text{reflux}]{\text{acetone}}$

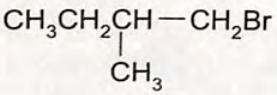
(j) $CH_3CH_2Br + Hg_2F_2 \longrightarrow$

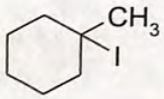
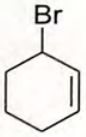
Solution

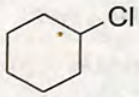
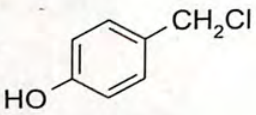
(a) 

(b) 

(c) 

(d) 

(e)  (f) 

(g)  (h) 

(i) CH_3CH_2I (j) CH_3CH_2F

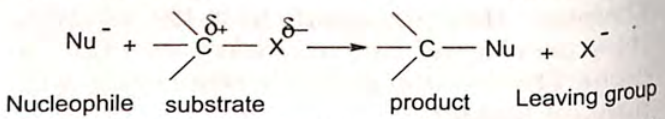
The experimental conditions are such that under (a), electrophilic bromination on the benzene ring; under (b), free radical benzylic bromination; under (c) and (e), Markownikov's addition; under (d), anti-Markownikov's addition; under (f), free radical allylic bromination; and under (i) and (j), halogen exchange occur. Under (g) and (h), the alcoholic group is replaced by chloro group. The phenolic group in (h) remains intact due to stronger C-O bond.

17.6 REACTIONS

The characteristic reactions of the halogen compounds are due to the presence of C-X bond in the molecule.

17.6.1 Nucleophilic Substitution Reactions

Due to the partial positive charge on the carbon atom bonded to the halogen in the organic halides, nucleophiles (Nu$^-$) displace the halogen as halide ion and form bond with the carbon. The organic halide is called the substrate and the departing halide ion, the leaving group.



It is one of the most extensively studied reactions of alkyl halides and other halides having C_{sp^3}-X bond. It is used to prepare a variety of organic compounds. Some of these reactions are given in Table 17.3.

Table 17.3 Nucleophilic Substitution of Alkyl Halides (R-X)

Nucleophile	Reagent	Substitution products	Class of main product
HO^-	NaOH (KOH)	ROH + NaX (KX)	Alcohol (hydrolysis)
R^1O^-	$NaOR^1$	ROR^1 + NaX	Ether (Williamson's ether synthesis)
I^-	NaI	R-I + NaX	Alkyl iodide
HS^-	NaSH	R-SH + NaX	Thiol
S^{2-}	Na_2S	RSR + NaX	Thioether
$R^1C{\equiv}C^-$	$R^1C{\equiv}CNa$	$RC{\equiv}CR^1$ + NaX	Alkyne
NH_3	NH_3	$R\text{-}NH_2.HX$	Amine hydrohalide
$^-C{\equiv}N$:	KCN (NaCN)	RCN + KX (NaX)	Nitrile (cyanide)
$^-C{\equiv}N$:	AgCN	RNC + AgX	Isonitrile (isocyanide)
$O{=}\ddot{N}\text{-}O^-$	KNO_2	R-O-N=O + KX	Alkyl nitrite
$O{=}\ddot{N}\text{-}O^-$	$AgNO_2$	$R\text{-}NO_2$ + AgX	Nitroalkane
R^1COO^-	R^1COONa	$ROCOR^1$ + NaX	Ester
H^-	$LiAlH_4$	$RH + AlX_3 + LiX$	Hydrocarbon

There are two nucleophilic centres, at carbon and nitrogen in cyanide ion($\overline{C} \equiv N:$), and at oxygen and nitrogen in nitrite ion ($O - \ddot{N} = O$). The nucleophliles with two nucleophilic centres are called **ambident nucleophiles**. They can react through either of these centres. Depending on the reagent and the reaction conditions, the reaction may take place predominantly at one of these centres.

For a given R group, the reactivity of the halide, R-X, follows the order opposite to the C–X bond dissociation energies. Thus,

RI > RBr > RCl >>> RF

In fact, the C-F bond is so strong that organic fluorides do not undergo nucleophilic substitution reactions under ordinary conditions.

Example 17.5

Give the structures of the main organic substitution product expected from the reaction of 1-bromobutane with
(a) $(CH_3)_3N$ (b) $(CH_3)_2S$ (c) CH_3COOAg
(d) $LiAlH_4$ (e) C_6H_5ONa

Solution

(a) $BuN^+(CH_3)_3Br^-$ (b) $BuS^+(CH_3)_2Br^-$
(c) $BuOCOCH_3$ (d) BuH
(e) $BuOC_6H_5$ (Bu = *n*-Butyl group)

Example 17.6

Give reagents, inorganic or organic, needed to convert benzyl bromide into
(a) benzyl iodide (b) benzyl ethyl ether
(c) benzyl alcohol (d) benzyl cyanide
(e) benzyl acetate (f) (nitromethyl)benzene
(g) tri-*n*-butylbenzylammonium bromide

Solution

(a) NaI (b) $NaOC_2H_5$ (c) NaOH (d) KCN
(e) $NaOCOCH_3$ (f) $AgNO_2$ (g) Bu_3N

Mechanism of nucleophilic substitution

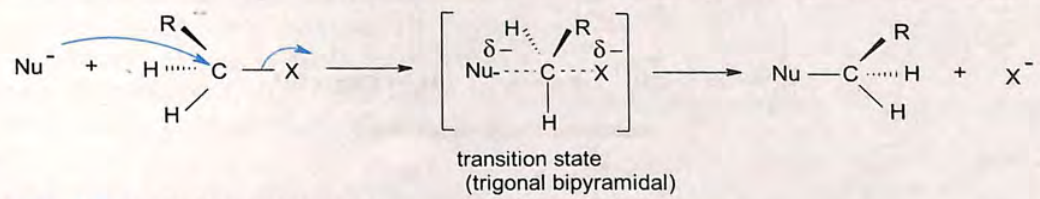
The nucleophilic substitution reactions in halides containing C_{sp3} –X bond can occur by either of the two mechanisms, S_N2 and S_N1.

(i) *S_N2 mechanism*: It occurs in one step. In this mechanism, the nucleophile, Nu^-, attacks the partially positive carbon of the C-X bond of the substrate from the backside of the C-X bond and the leaving group, X^-, departs simultaneously (Scheme 17.1).

(ii) *S_N1 mechanism*: It occurs in two steps. In step 1, the polarised C-X bond undergoes slow heterolysis to produce a carbocation (also called carbonium ion) and a halide anion. A carbocation is highly reactive electrophilic species of low stability. Therefore, the carbocation rapidly reacts with the nucleophile in step 2 to complete the substitution reaction (Scheme 17.2). Step 1 is slow compared to step 2 as the former requires energy for the cleavage of the C-X bond whereas the latter releases energy due to the formation of the C –Nu bond. S_N1 mechanism is facilitated by polar protic solvents, such as water, alcohol or aqueous-organic solvents. Such solvents promote the ionisation step by stabilizing the ions by solvation (see Unit 8 also).

Nucleophilic substitution seldom occurs exclusively by one mechanism only. With a given halogen, primary, secondary and tertiary halides show opposite orders of reactivity in the two mechanisms.

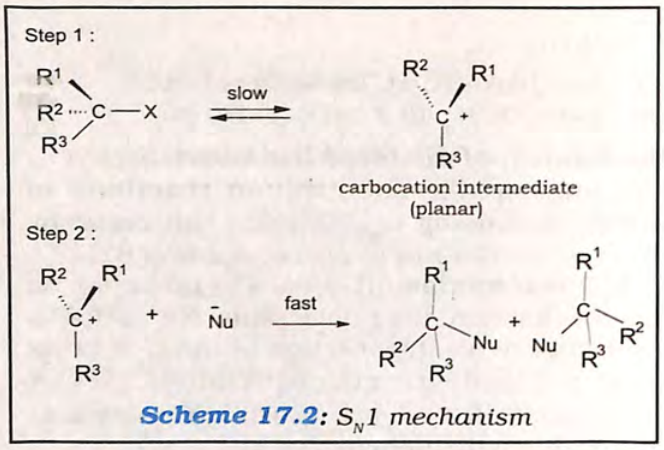
An alkyl group at the α-carbon, being bigger in size than the hydrogen atom, tends to block the approach of the nucleophile to this carbon (steric hindrance) in the S_N2 mechanism and



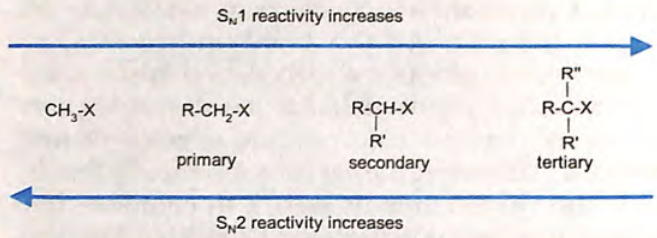
transition state
(trigonal bipyramidal)

Scheme 17.1: S_N2 mechanism
The dotted lines of the species in the square bracket called transition state indicate the bonds, which are in the process of being formed or broken.

* *S= Substitution, N= Nucleophilic, 2= Bimolecular, 1= Unimolecular. Molecularity of a reaction is the number of molecules taking part in the slowest step.*



Scheme 17.2: *S_N1 mechanism*



makes the reaction difficult to occur. In the S_N1 mechanism, a carbocation is formed in the difficult slow step marked, step 1. The more stable the carbocation intermediate, the more easily it is formed, and thus, the easier is the overall reaction to occur. As you know (Unit 14), the stability of a carbocation increases in the following order:

$$\overset{+}{C}H_3 < \overset{+}{R}\text{-}CH_2 < \text{R-CH}^{+}(\text{R}) < \text{R-C-R}^{+}(\text{R}')$$

primary secondary tertiary

Primary allylic and primary benzylic halides show higher reactivity in S_N1 reactions than other primary alkyl halides This is due to greater stabilisation of the allylic and benzylic carbocation intermediates by resonance.

Thus, primary alkyl halides almost always react predominantly by S_N2 mechanism whereas tertiary alkyl halides react predominantly by S_N1 mechanism. Secondary alkyl, primary allylic and primary benzylic halides may react predominantly by either mechanism, or by both the mechanisms without much preference, depending on the nature of the nucleophile and the solvent. A detailed discussion of this is beyond the scope of this book.

Example 17.7

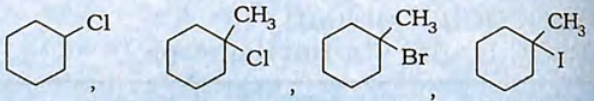
Arrange the following halides in order of increasing S_N2 reactivity:
CH_3Cl, CH_3Br, CH_3CH_2Cl, $(CH_3)_2CHCl$

Solution

$(CH_3)_2CHCl < CH_3CH_2Cl < CH_3Cl < CH_3Br$
As the size of the alkyl group increases, the S_N2 reactivity decreases. Further, C-Cl bond is stronger and more difficult to cleave than C-Br bond.

Example 17.8

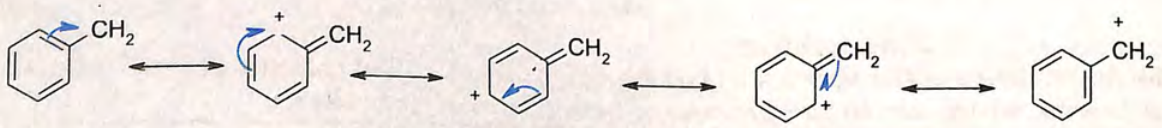
Predict the order of reactivity of the following compounds in S_N1 reactions:



Solution

First compound is a secondary halide and the other three are tertiary halides. Also the reactivity follows the order chloride < bromide < iodide. Thus, the compounds as given are arranged in increasing order of reactivity in S_N1 reactions.

resonance in allyl carbocation



resonance in benzyl carbocation

Example 17.9
Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions:
(a) The four isomeric bromobutanes
(b) $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)$-Br, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

Solution

(a) $CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH(Br)CH_3 < (CH_3)_3CBr$ (S_N1)

$CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > CH_3CH_2CH(Br)CH_3 > (CH_3)_3CBr$ (S_N2)

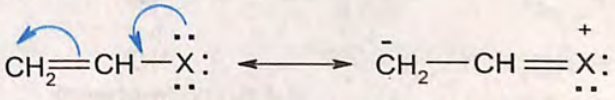
Of the two primary bromides, the carbocation intermediate derived from $(CH_3)_2CHCH_2Br$ is more stable than that derived from $CH_3CH_2CH_2CH_2Br$ because of greater electron donating inductive effect of $(CH_3)_2CH$- group. Therefore, $(CH_3)_2CHCH_2Br$ is more reactive than $CH_3CH_2CH_2CH_2Br$ in S_N1 reactions. $CH_3CH_2CH(Br)CH_3$ is a secondary bromide and $(CH_3)_3CBr$ is a tertiary bromide. Hence, the above order in S_N1. The reactivity in S_N2 reactions follows the reverse order as the steric hindrance around the electrophilic carbon increases in that order.

(b) $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)$-Br $> C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$ (S_N1)

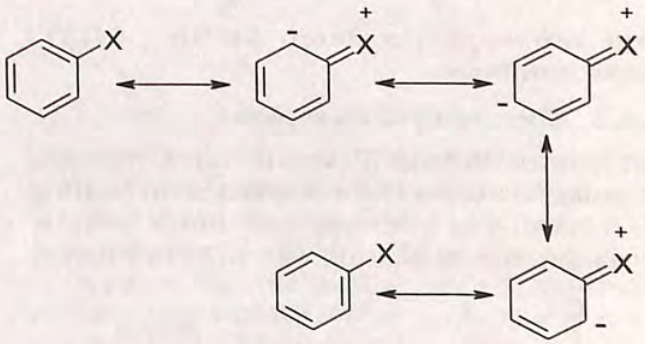
$C_6H_5C(CH_3)(C_6H_5)Br < C_6H_5CH(C_6H_5)$-Br $< C_6H_5CH(CH_3)Br < C_6H_5CH_2Br$ (S_N2)

Of the two secondary bromides, the carbocation intermediate obtained from $C_6H_5CH(C_6H_5)$-Br is more stable than that obtained from $C_6H_5CH(CH_3)Br$ because it is stabilized by two phenyl groups due to resonance. Therefore, the former bromide is more reactive than the latter in S_N1 reactions. A phenyl group is bulkier than a methyl group. Therefore, $C_6H_5CH(C_6H_5)$-Br is less reactive than $C_6H_5CH(CH_3)Br$ in S_N2 reactions.

Vinylic and aryl halides are unreactive in nucleophilic substitution reactions under the conditions under which alkyl halides react. This is because of resonance effect. Resonance gives rise to partial double bond character to the carbon-halogen bond, making it stronger and, therefore, more difficult to cleave than a C_{sp^3}–X bond. It also reduces the polarity of the carbon-halogen bond, thereby making the heterolysis of the C-X bond difficult.

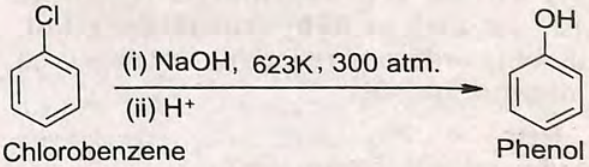


resonance in vinyl halide

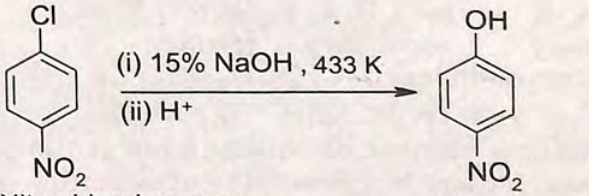


resonance in halobenzene

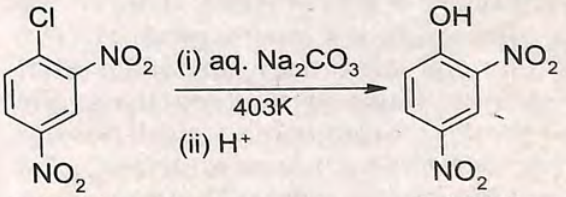
Halobenzenes, however, become reactive to nucleophilic substitution when electron-withdrawing groups (nitro,cyano,etc.) are present at *ortho* and/or *para* positions. As the number of such groups increases the reactivity increases. This is clear from the progressively milder reaction conditions required for hydrolysis in going from chlorobenzene to 2,4,6-trinitrochlorobenzene as shown below:



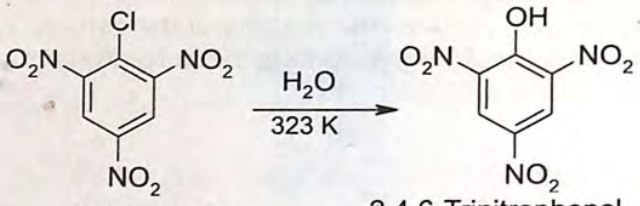
Chlorobenzene — Phenol



p-Nitrochlorobenzene — p-Nitrophenol



2,4-Dinitrochlorobenzene — 2,4-Dinitrophenol



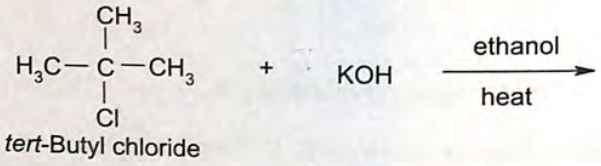
2.4.6-Trinitro-chlorobenzene

2,4,6-Trinitrophenol (picric acid)

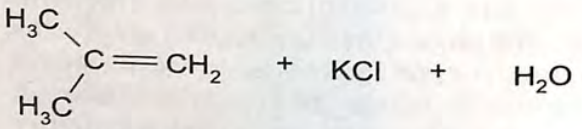
Other nucleophiles (such as NH_3, CH_3O^-) behave similarly.

17.6.2 Elimination Reactions

Alkyl halides undergo β-elimination of hydrogen and halogen atoms to form alkenes on heating with a base. For example, *tert*- butyl chloride gives isobutene on heating with KOH in ethanol.



tert-Butyl chloride



Isobutene

Such a reaction in which hydrogen and halogen atoms are eliminated from the reactant is known as **dehydrohalogenation**. The following orders of reactivity are observed in the organic halides:

RCl < RBr < RI

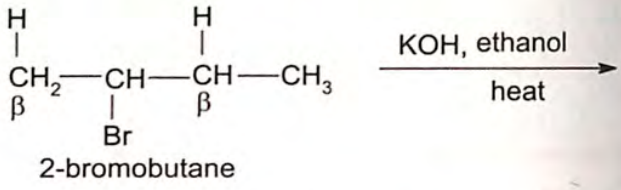
for a given organic group, and

RCH_2-X < RR′CH-X < RR′R″C-X

primary secondary tertiary

for a given halogen.

The reactivity also increases with increasing number of substituents at the β-carbon. If there is a possibility of formation of more than one alkene due to the availability of different types of β-hydrogens, usually one of these alkenes is the major product. The Russian chemist Alexander Saytzeff stated that *in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.* This has come to be known as **Saytzeff rule**. Thus, 2-bromobutane gives but-2-ene as the major product on heating with KOH in ethanol.



2-bromobutane

$CH_3CH=CHCH_3$ + $CH_2=CHCH_2CH_3$

But-2-ene But-1-ene

81% (major product) 19% (minor product)

Example 17.10

Identify all the possible alkenes that would be formed on dehydrohalgenation of the following organic halides with alcoholic KOH. Also identify the major alkene.

(a) 1-Chloropentane
(b) 2-Chloropentane
(c) 2-Chloro-2-methylbutane
(d) 2-Chloro-3-methylbutane
(e) 3-Chloro-2- methylpentane

Solution

(a) Pent-1-ene (b) Pent-1-ene, Pent-2-ene (major) (c) 2-Methylbut-1-ene, 2-Methylbut-2-ene (major) (d) 3-Methylbut-1-ene, 2-Methylbut-2-ene (major) (e) 2-Methylpent-2-ene (major), 4-Methylpent-2-ene.

According to Saytzeff rule, the more substituted alkene is the major product.

Example 17.11

Write steps to bring about the following transformations in not more than two steps.

(a) Acetylene to pent-2-yne
(b) *tert*-Butyl bromide to isobutyl bromide
(c) Butan-1-ol to but-1-ene

Solution

(a) $CH \equiv CH \xrightarrow[\text{then } CH_3I]{Na(1 \text{ equiv.})/NH_3(l)} CH \equiv C-CH_3$

Acetylene Propyne

$\xrightarrow[\text{then } CH_3CH_2Br]{Na/NH_3(l)} CH_3CH_2C \equiv C-CH_3$

Pent-2-yne

(b) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \xrightarrow[\text{heat}]{\text{KOH / ethanol}} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{peroxide}]{\text{HBr}} H\,C_3-\overset{\overset{CH_3}{|}}{CH}-CH_2Br$

tert - Butyl bromide — Isobutene — Isobutyl bromide

(c) $CH_3CH_2CH_2CH_2\text{-}OH \xrightarrow[H_2SO_4,\ \text{heat}]{NaBr} CH_3CH_2CH_2CH_2Br \xrightarrow[\text{ethanol, heat}]{KOH} CH_3CH_2CH{=}CH_2$

Butan-1-ol — 1- Bromobutane — But-1-ene

Direct acid– catalysed dehydration (Unit 15) of butan-1-ol will give but-2-ene as the major alkene.

17.6.3 Reactions with metals

Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as **organometallic compounds**. An important class of organometallic compounds constitutes the **Grignard reagents**, named after their discoverer, Victor Grignard, a French chemist who received the Nobel Prize in chemistry in 1912. Grignard reagents are obtained by the reaction of alkyl halides with magnesium in dry ether.

$$R\text{-}X + Mg \xrightarrow{\text{dry ether}} RMgX \quad (X = Cl, Br, I)$$

alkyl magnesium halide (Grignard reagent)

Vinyl and aryl halides also form Grignard reagents. Grignard reagents are highly reactive. They react with any source of proton to give hydrocarbons. Even water, alcohols, amines, terminal alkynes etc. are sufficiently acidic to convert them to the corresponding hydrocarbon.

$$RMgX + ZH \longrightarrow RH + ZMgX$$

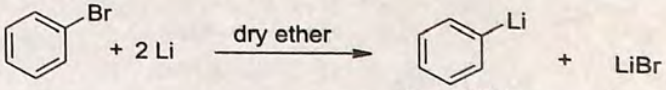
(Z= OH, RO, NH_2, RNH, $RC{\equiv}C$)

It is, therefore, necessary to avoid even traces of moisture from a Grignard reagent. On the other hand, this could be a method to reduce the halides to hydrocarbons. Grignard reagents also react with oxygen and carbon dioxide. Therefore, they should be prepared and used in the absence of air under inert atmosphere. Grignard reagents are very useful for the preparation of a number of organic compounds.

Organic halides also form organometallic compounds when treated with alkali metals (Li, Na, K). They behave like Grignard reagents.

$$CH_3CH_2CH_2CH_2Br + 2Li \xrightarrow{\text{dry ether}} CH_3CH_2CH_2CH_2Li + LiBr$$

Butylithium



Phenyllithium

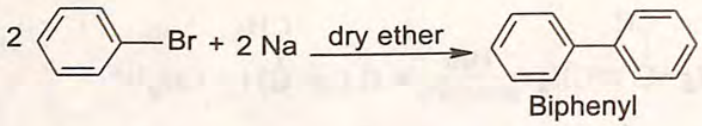
Alkyl halides react with sodium in dry ether to give a hydrocarbon containing double the number of carbon atoms present in the halide. This reaction is known as **Wurtz reaction**.

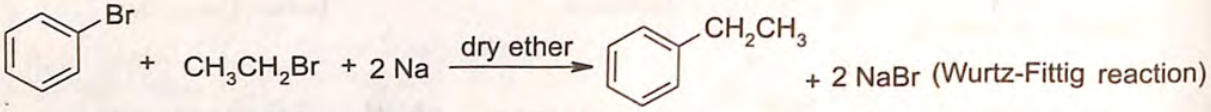
$$2RX + 2Na \xrightarrow{\text{dry ether}} R-R + 2NaX$$

This reaction generally fails with tertiary alkyl halides. When a mixture of two different alkyl halides is used, all the three possible alkanes are formed.

$$R^1X + R^2X + Na \xrightarrow{\text{dry ether}} R^1R^1 + R^2R^2 + R^1R^2 + NaX$$

Aryl halides also give analogous compounds in which two aryl groups are joined together **(Fittig reaction)**. A mixture of an alkyl halide and an aryl halide gives an alkylarene **(Wurtz-Fittig reaction)**. Alkane and biaryl are also formed as by products in the Wurtz-Fittig reaction.

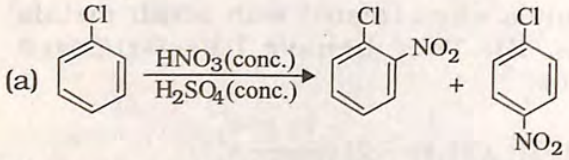




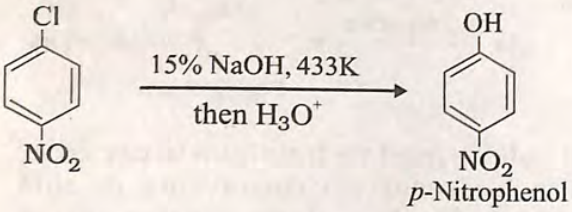
Example 17.12

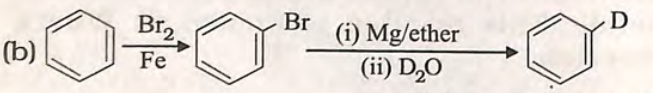
How will you effect the following two-step conversions?
(a) chlorobenzene to p-nitrophenol
(b) benzene to monodeuteriobenzene

Solution



The mixture of the products is separated by fractional crystallisation and the *para* isomer is used in the next step as follows:





(via Grignard reagent)

17.7 POLYHALOGEN COMPOUNDS

Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture. Some important polyhalogen compounds are described in this section.

Dichloromethane (Methylene chloride): It is prepared industrially by direct chlorination of methane. The mixture so obtained is separated by fractional distillation. It is a colourless, sweet-smelling, volatile liquid, b.p. 313K. Because of its low b.p. and low inflammability, it is an effective extraction solvent used in pharmaceutical and food industries.

Trichloromethane (Chloroform): It is manufactured by chlorination of methane followed by separation by fractional distillation. It is a sweet-smelling liquid, b.p. 334K. It is widely used in industry as a solvent for fats, waxes, resins, rubber, etc. It was once used as an anaesthetic in surgery and as flavouring agent in cough syrups but it is now known to be too toxic for such uses. Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas carbonyl chloride, also known as phosgene. It is, therefore, stored in closed dark

Francois Auguste Victor Grignard was born in Cherbourge, France on May 6, 1871. He joined the secondary school of his native place where he distinguished himself among his co-students. He was rewarded for his efforts by the 'prize of excellence' every year from 1883 to 1887. He received a degree in mathematics but switched to chemistry and got his Ph.D. degree at the university of Lyon in 1901. During his doctoral work under Phillipe Barbier, Grignard discovered the preparation and usefulness of organomagnesium reagents. He first reported his work on these reagents in 1910. In the same year he became Professor of chemistry at the university of Nancy. He won the Nobel prize in chemistry in 1912 jointly with Paul Sabatier who had worked on nickel-catalysed hydrogenation. During World War I, he was drafted into the French army as a Corporal, when he developed a method for detecting German war gases. He died at the age of 64 on December 13, 1935.

Francois Auguste Victor Grignard (1871-1935)

coloured bottles completely filled so that air is kept out.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl$$
Phosgene

On warming with silver powder, chloroform is converted into ethyne.

$$2\,CHCl_3 + 6\,Ag \longrightarrow HC \equiv CH + 6\,AgCl$$

Carbylamine (isocyanide) test: When chloroform is heated with ethanolic potassium hydroxide and a primary amine (e.g. ethyl amine or aniline), an isocyanide (carbylamine) is formed, which is easily detected by its nauseating odour.

$$CHCl_3 + RNH_2 + 3KOH \rightarrow RN^+ \equiv C^- + 3KCl + 3H_2O$$
Carbylamine

When treated with nitric acid, chloroform forms nitrochloroform, also known as chloropicrin. Chloropicrin is an insecticide. It has also been used as a war gas.

$$CHCl_3 + HNO_3 \longrightarrow Cl_3CNO_2 + H_2O$$
Chloropicrin

Chloroform adds on acetone in the presence of potassium hydroxide to give chloretone, which is used as a hypnotic drug.

$$CHCl_3 + CH_3COCH_3 \xrightarrow{KOH} (H_3C)_2C(OH)CCl_3$$
Chloretone

Triiodomethane (Iodoform): It is prepared by heating ethanol or acetone with sodium hydroxide and iodine or sodium carbonate and iodine in water. Iodoform, being insoluble in water precipitates as a yellow solid. The reaction is known as **iodoform reaction**.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 6NaOH + 4I_2 \xrightarrow{\text{heat}} \underset{\text{Iodoform}}{CHI_3} + HCOONa + 5H_2O + 5NaI$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 4NaOH + 3I_2 \xrightarrow{\text{heat}} CHI_3 + CH_3COONa + 3H_2O + 3NaI$$

The reactions occur in the following steps.

$$2NaOH + I_2 \rightarrow \underset{\text{Sodium hypoiodite}}{NaOI} + NaI + H_2O$$

$$CH_3CH_2OH + NaOI \rightarrow CH_3CHO + NaI + H_2O$$

$$CH_3CHO + 3NaOI \rightarrow \underset{\text{Triiodoacetaldehyde}}{I_3CCHO} + 3NaOH$$

$$I_3CCHO + NaOH \rightarrow CHI_3 + \underset{\text{Sodium formate}}{HCOONa}$$

$$CH_3COCH_3 + 3NaOI \rightarrow \underset{\text{Triiodoacetone}}{I_3CCOCH_3} + 3NaOH$$

$$I_3CCOCH_3 + NaOH \rightarrow CHI_3 + \underset{\text{Sodium acetate}}{CH_3COONa}$$

Other compounds which contain the structural unit $CH_3CH(OH)$- or $CH_3C{=}O$ bonded to a carbon or hydrogen atom, also give yellow precipitate of iodoform. Therefore, this reaction is of diagnostic value and is used in qualitative analysis to detect the presence of these structural units. In this application, the reaction is known as **iodoform test.**

Iodoform is a yellow solid, mp (392K). It is insoluble in water but readily soluble in ethanol and ether. Its chemical properties are similar to those of chloroform. It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

Chlorine and bromine can replace iodine in iodoform reaction to give chloroform and bromoform, respectively. In this generalised form, the reaction is known as **haloform reaction**. In the chloroform reaction, it is more convenient and less expensive to use bleaching powder in place of chlorine and alkali. Bleaching powder serves as a source of chlorine and calcium hydroxide. Calcium hydroxide brings about the cleavage of the trichloro derivative in the final step of the reaction.

Activity

Warm a solution of 10g of sodium carbonate in 50 mL of water and 5 mL of ethanol taken in a china dish or beaker to about 343K on a water bath. Add iodine to the solution in portions till a permanent reddish tinge is obtained (about 5 g of iodine is required). Add a few drops of sodium hydroxide to discharge the colour. Cool and filter the yellow solid. Wash the solid thoroughly on filter paper with water to remove alkali and dry. Recrystallise the yellow solid from ethanol to get pure iodoform. Determine its melting point.

Tetrachloromethane (Carbon tetrachloride): It is prepared industrially by chlorination of methane and by the action of chlorine on carbon disulphide in the presence of aluminium chloride as catalyst.

$$\underset{\text{Carbon disulphide}}{CS_2} + 3Cl_2 \xrightarrow{AlCl_3} CCl_4 + \underset{\text{Suphur monochloride}}{S_2Cl_2}$$

Carbon tetrachloride is a colourless liquid, b.p. 350K. It has a sickly smell. It is widely used as an industrial solvent for oils, fats, resins, lacquers, etc. It is non-flammable and is used as a fire extinguisher. It is stable at red heat (about 773K). At this temperature, it is hydrolysed by water vapour to some extent to form phosgene. Therefore, after using it to extinguish fire the room should be well ventilated.

$$CCl_4 + H_2O \xrightarrow{773K} COCl_2 + 2HCl$$

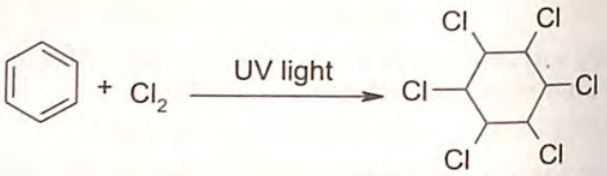
p-Dichlorobenzene: It is prepared by chlorination of benzene. It is a white, volatile solid, m.p. 325K, which readily sublimes. It is used as a general insecticide, germicide, soil fumigant deodorant and moth repellent.

Freons: The chlorofluoro compounds of methane and ethane are collectively known as Freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Dichlorodifluoromethane (CCl_2F_2, Freon 12) is one of the most common Freons in industrial use. It is manufactured from tetrachloromethane by Swarts reaction. Freons are used as

$$3CCl_4 + 2SbF_3 \xrightarrow{\text{heat}} \underset{\text{Freon 12}}{3CCl_2F_2} + 2SbCl_3$$

refrigerants in refrigerators and air conditioners hence the name Freons. They have also been used extensively as propellants for aerosols and foams to spray out deodorants, cleansers, hair sprays, shaving creams, insecticides, etc. It is now established that Freons deplete the protective ozone layer surrounding our planet (Unit 18). Therefore, the use of Freons as propellants and refrigerants has been drastically curtailed or banned in many countries.

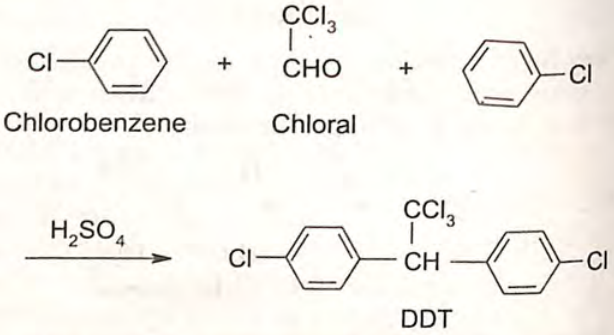
Benzene hexachloride (BHC): The trade names of benzene hexachloride are lindane and gammaxane. It is commercially prepared by the addition of chlorine to benzene in the presence of ultraviolet light. It is used as a pesticide in agriculture. It is a mixture of several isomers, out of which the gamma isomer (Gammaxane) is responsible for the pesticidal activity.



Benzene hexachloride

p,p'– Dichlorodiphenyltrichloroethane (DDT): It is manufactured by condensation of chlorobenzene with trichloroacetaldehyde (chloral) in the presence of sulphuric acid.

It is a white powder insoluble in water but soluble in oils. It is a powerful insecticide. However, it is highly stable and is not easily decomposed in the environment. Therefore, its long-term effects could be potentially dangerous and its use is banned in many countries.



Perfluorocarbons (PFC's): Perfluorocarbons, C_nF_{2n+2}, are obtained by controlled fluorination of vaporized alkanes diluted with nitrogen gas in the presence of a catalyst.

$$C_7H_{16} + 16F_2 \xrightarrow[CoF_2\text{(Catalyst)}]{\text{vapour phase, } N_2, 573K} \underset{\text{Perfluoroheptane}}{C_7F_{16}} + 16HF$$

Perflurocarbons are colourless, odourless, non-toxic, non-flammable, non-corrosive, nonpolar, extremely stable and unreactive gases, liquids or solids. They are stable to ultraviolet light and other ionising radiations, and therefore, do not deplete the ozone layer. They are good electrical insulators. They are used as lubricants, surface coatings, dielectrics, heat transfer media in high voltage electrical equipment etc. In electronic industry, they are

used for vapour phase soldering, gross leak detection of sealed microchips, etc. They find several applications in health care and medicine, e.g., in skin care cosmetics, wound healing, liquid ventilation, retina reattachment, carbon monoxide poisoning and medical diagnosis.

SUMMARY

Organic halogen compounds are derivatives of saturated and unsaturated hydrocarbons. They are prepared by **free radical halogenation** of hydrocarbons or by **electrophilic halogenation** of arenes, by electrophilic addition of halogens or hydrogen halides to alkenes or alkynes, and by replacement of the hydroxy group of alcohols by halogens using halogen acids, phosphorus halides or thionyl chloride. Fluorides and, in some cases, iodides are prepared by halogen exchange methods. Chlorides, bromides and iodides undergo nucleophilic **substitution** and **elimination reactions** and **form organometallic compounds**. Through these reactions, a variety of useful classes of organic compounds can be prepared. The C-X bond being polar is the site for nucleophilic substitution reactions, which can take place by $\mathbf{S_N2}$ or $\mathbf{S_N1}$ mechanism depending upon the structure of the halide and reaction conditions. Halides containing C_{sp^2}–X bond are unreactive under comparable conditions. Electron withdrawing groups at *ortho* and *para* positions increase the reactivity of aryl halides in nucleophilic substitution reactions. A number of polyhalogen compounds, e.g. dichloromethane,haloforms, carbon tetrachloride, *p*-dichlorobenzene, Freons, BHC, DDT and PFC's have many industrial applications. Some of these compounds are not easily decomposed in the environment. Therefore, their indiscriminate use is discouraged.

EXERCISES

17.1 Name the following halides according to IUPAC system and classify them as alkyl, allylic, benzylic (primary, secondary, tertiary), vinylic or aryl halides:

(a) $(CH_3)_2CHCH(Cl)CH_3$ (b) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$ (c) $CH_3CH_2C(CH_3)_2CH_2I$

(d) $(CH_3)_3CCH_2CH(Br)C_6H_5$ (e) $CH_3CH(CH_3)CH(Br)CH_3$ (f) $CH_3C(Cl)(C_2H_5)CH_2CH_3$

(g) $CH_3C(C_2H_5)_2CH_2Br$ (h) $CH_3CH{=}C(Cl)CH_2CH(CH_3)_2$ (i) $CH_3CH{=}CHC(Br)(CH_3)_2$

(j) *p*-$ClC_6H_4CH_2CH(CH_3)_2$ (k) *m*-$ClCH_2C_6H_4CH_2C(CH_3)_3$ (l) *o*-Br-$C_6H_4CH(CH_3)CH_2CH_3$

17.2 Give the IUPAC names of the following compounds:

(a) $CH_3CH(Cl)CH(Br)CH_3$ (b) $CHF_2CBrClF$ (c) $ClCH_2C \equiv CCH_2Br$ (d) $(CCl_3)_3CCl$

(e) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$ (f) $(CH_3)_3CCH{=}C(Cl)C_6H_4I$-*p* (g)$CH_3CHCl(CH_2)_2CCl_2C_2H_5$

17.3 Write the structure of the following organic halogen compounds.
(a) 2-Chloro-3-methylpentane (b) *p*-Bromochlorobenzene (c) 1-Chloro-4-ethylcyclohexane (d) 2-(2-Chlorophenyl)-1-iodooctane (e) Perfluorobenzene (f) 4-*tert*-Butyl-3-iodoheptane (g) 1-Bromo- 4-*sec*-butyl–2-methybenzene (h) 1,4-Dibromobut-2-ene.

17.4 A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

17.5 A hydrocarbon C_5H_{12} gives only one monochlorination product. Identify the hydrocarbon.

17.6 Write the equations for the preparation of 1-iodobutane from:
(a) 1-Butanol (b) 1-Chlorobutane (c) But-1-ene

17.7 What are ambident nucleophiles? Explain with an example.

17.8 Outline the preparation of the following compounds using a nucleophilic substitution reaction.

(a) $CH_3OC(CH_3)_3$ (b) $CH_3C{\equiv}CCH_2CH_3$ (c) $CH_3CH_2CH_2N(CH_3)_2$ (d) $C_6H_5CH_2OCOCH_3$

(e) $CH_3CH_2CH_2CH_2NO_2$ (f) $CH_3CH_2CH_2CN$ (g) $C_6H_5CH_2N^+{\equiv}C^-$ (h) CH_3CH_2-O-N=O

17.9 Which compound in each of the following pairs will react faster in S_N2 reaction with HO^-?

(a) CH_3Br or CH_3I (b) $(CH_3)_3CCl$ or CH_3Cl (c) CH_2=CHBr or CH_2=CH-CH_2Br

17.10 Arrange the following compounds in increasing order of S_N1 reactivity.

(a) $ClCH_2CH{=}CHCH_2CH_3$, $CH_3C(Cl){=}CHCH_2CH_3$, $CH_3CH{=}CHCH_2CH_2Cl$, $CH_3CH{=}CHCH(Cl)CH_3$

(b) CH_3CH_2Br, $CH_2{=}CHCH(Br)CH_3$, $CH_2{=}CHBr$, $CH_3CH(Br)CH_3$

(c) $(CH_3)_3CCl$, $C_6H_5C(CH_3)_2Cl$, $(CH_3)_2CHCl$, $CH_3CH_2CH_2Cl$

17.11 Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene.
(a) 1-Bromo-1-methylcyclohexane (b) Cyclohexylmethyl bromide (c) 2-Chloro-2-methylbutane (d) 3-Bromopent-1-ene (e) 2,2,3-Trimethyl-3-bromopentane.

17.12 Predict the order of reactivity of the following compounds in dehydrohalogenation:

(a) $CH_3CH_2CH_2CH_2Cl$,$(CH_3)_2CHCH_2Cl$,$(CH_3)_2CH$-CH_2Br,$CH_3CH(Br)CH_2CH_3$,$(CH_3)_3C$-Br

(b) $CH_3CH(Br)CH_3$, $CH_3CH_2CH_2Br$, $(CH_3)_2CH$-CH_2Br, $(CH_3)_3$ C-CH_2Br

17.13 How will you bring about the following conversions in not more than two steps?

(a) Ethanol to But-1-yne
(b) Ethene to Bromoethene
(c) Propene to 1-Nitropropane
(d) Toluene to Benzyl alcohol
(e) Propene to Propyne
(f) Ethanol to Ethyl fluoride
(g) Bromomethane to Propanone
(h) But-1-ene to But-2-ene
(i) 1-Chlorobutane to *n*-Octane
(j) Bromoethane to *cis*-Hex-3-ene
(k) Benzyl alcohol to Phenylethanenitrile
(l) Benzene to Biphenyl
(m) Cyclopentene to Cyclopenta-1,3-diene
(n) Aniline to Phenyl isocyanide

17.14 An alkyl chloride (A), on reaction with magnesium in dry ether followed by treatment with ethanol gave 2-methylbutane. Write all the possible structures of (A).

17.15 Which of the following compounds will give positive iodoform test? Butan-1-ol, Butan-2-ol, *tert*-Butyl alcohol, Ethanal, Propanal, Propanone, Butan-2-one, Pentan-3-one, Cyclohexanone, 1-Methylcyclohexanol, 1-Phenylethanol, 2-Phenylethanol.

17.16 How will you distinguish between:

(a) Methanol and Ethanol,
(b) Propan-1-ol and Propan-2-ol,
(c) Benzyl chloride and Chlorobenzene
(d) *n*-Butyl amine and Diethyl amine

17.17 Explain why,

(a) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
(b) alkyl halides, though polar, are immiscible with water.
(c) vinyl chloride is unreactive in nucleophilic substitution reactions.
(d) neopentyl bromide undergoes nucleophilic substitution reactions very slowly.
(e) 3-bromocyclohexene is more reactive than 4-bromocyclohexene in hydrolysis with aqueous NaOH.
(f) *tert*-butyl chloride reacts with aqueous sodium hydroxide by S_N1 mechanism while *n*-butyl chloride reacts by S_N2 mechanism.
(g) Grignard reagents should be prepared under anhydrous conditions.

17.18 Give the preparation and uses of chloropicrin, chloretone, Freon12, *p*-dichlorobenzene, BHC, DDT, carbon tetrachloride, iodoform, , perfluorocarbons.

17.19 The nucleophilic substitution of primary alkyl chlorides with sodium acetate is catalysed by sodium iodide. Explain why?

17.20 In each of the following reactions, a new ring is formed. Use curved arrow notations to explain the formation of the new ring.
(a) 1,4-Dibromobutane (0.1 mol) is treated with sodium sulphide (0.1 mol) in aqueous ethanol.
(b) 1-Chloro-2-(2-hydroxyphenyl)ethane is treated with aqueous sodium hydroxide. *(Hint:* Phenols are converted into phenoxides by treatment with NaOH solution)

17.21 *p*-Methoxylbenzyl bromide reacts faster than *p*-nitrobenzyl bromide with ethanol to form an ether product. Explain why.

17.22 Explain the formation of the two products in the following reaction:

$CH_3CH{=}CHCH_2Cl + H_2O \rightarrow CH_3CH{=}CHCH_2OH + CH_3CH(OH)CH{=}CH_2$

17.23 What mass of propene is obtained from 34.0g of 1-iodopropane on heating with ethanolic KOH, if the yield is 36% ?

17.24 An excess of methylmagnesium iodide reacts with 0.6g of an organic compound $C_3H_6O_3$ to evolve 295.7 mL of methane gas at S.T.P. Calculate the number of active hydrogen atoms in the molecule of the organic compound.

17.25 Write the structure of the major organic product in each of the following reactions:

(a) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}}$ (b) $(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

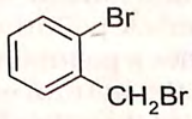
(c) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{water}}$ (d) $CH_3CH_2Br + KCN \xrightarrow{\text{aq. ethanol}}$

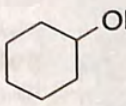
(e) $(CH_3)_3CBr + H_2O \xrightarrow{\text{heat}}$ (f) $(CH_3)_2CH - CH(Br)CH_2CH_3 \xrightarrow[\text{ethanol/heat}]{C_2H_5ONa}$

(g) $CH_3CH_2Cl + SbF_3 \xrightarrow{\text{heat}}$ (h) $CH_2{=}CHCH_2Br + CH_3C{\equiv}CNa \xrightarrow{\text{liq. } NH_3}$

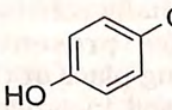
(i) $C_6H_5CH_2Cl + C_2H_5ONa \rightarrow$ (j) $CH_3CH_2CH_2OH + SOCl_2 \rightarrow$

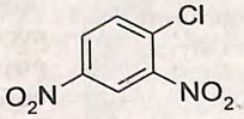
(k) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}}$ (l) $CH_3CH{=}C(CH_3)_2 + HBr \rightarrow$

(m) 

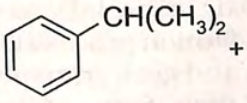
+ NaSH ⟶ (n) 

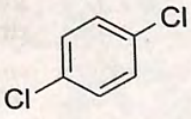
red P/I_2 ⟶

(o) 

+ HBr ⟶ (p) 

+ C_2H_5ONa $\xrightarrow[\text{heat}]{\text{ethanol}}$

(q) 

+ Br_2 $\xrightarrow{\text{heat}}$ (r) 

+ HNO_3 $\xrightarrow{H_2SO_4}$

UNIT 18

ENVIRONMENTAL CHEMISTRY

"Do no dishonour to the earth, lest you dishonour the spirit of man"

Objectives

After studying this Unit, you will be able to

- know the meaning and scope of environmental chemistry.
- learn about atmospheric pollution, depletion of ozone layer; acid rain, greenhouse effect, mists, smoke, fumes, dust and smogs.
- know about water pollution: major pollutants, international standards for drinking water, biochemical oxygen demand (BOD) and chemical oxygen demand (COD); land pollution: major pollutants and pesticides.
- appreciate the necessity of control of environmental pollution through the management of waste and green chemistry.

Chemistry plays a major role in our environment. There are many chemical species in our environment which cause a large number of chemical phenomena. **Environmental chemistry** is the science of these chemical phenomena. In a broader sense, it deals with the study of the origin, transport, reactions, effects and fates of chemical species in the environment. In this unit, we shall be studying some important topics in the field of environmental chemistry with special reference to pollution of air, water and land and some interesting chemical phenomena.

18.1 ENVIRONMENTAL POLLUTION

Environmental pollution may be described as the contamination of the environment with harmful wastes arising mainly from certain human activities. These activities release into the environment certain materials which pollute the atmosphere, water and soil. The effects of pollution are increasing at a fast rate and if the same are not checked and controlled, human existence and habitat would be in peril.

Any substance, which causes pollution, is known as a **pollutant**. A substance becomes a pollutant when it is present in concentrations harmful to the natural environment. Often only highly toxic substances are thought of as pollutants, but even substances that are normally considered harmless can cause pollution if they are present in undesirable concentrations and in the wrong place at the wrong time. For example, nitrate is added to soil in order to increase plant growth, but an excessive concentration of nitrate present in drinking water can be toxic, especially to young children.

In an environmental pollution process (Fig. 18.1) a pollutant originates from a source and gets transported by air or water or is dumped on land by man. Some of the pollutants may be absorbed (assimilated) or chemically changed by the environment; the rest build up to concentrations which are harmful to the environment.

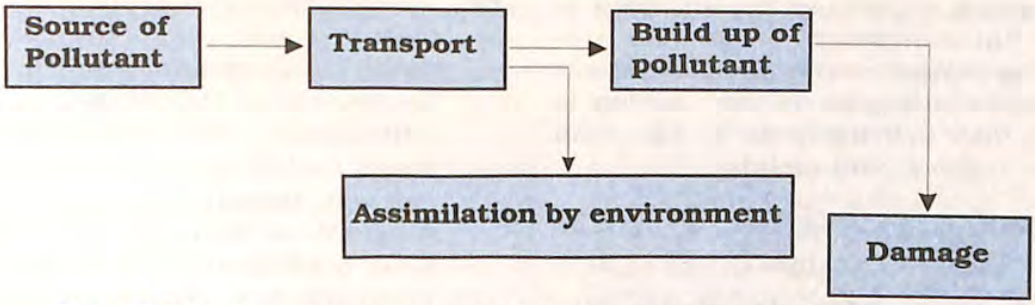


Fig. 18.1 A schematic representation of an environmental pollution process

18.2. ATMOSPHERIC POLLUTION

Atmosphere, which envelopes the earth, is divided into different layers or regions. The lowest region, called the **troposphere,** extends up to the height of ~10 km from sea level. Above the troposphere, between 10 and 50 km above sea level, lies the **stratosphere**. The troposphere contains about 80% of the total mass of air and almost all of the water vapours. The stratosphere, on the other hand, contains nitrogen, oxygen and ozone. Atmospheric pollution is generally studied under two heads: **Tropospheric pollution and Stratospheric pollution**. Since only a few substances produced by human activity reach the stratosphere, its pollution results in the depletion of the ozone layer which causes biologically harmful ultraviolet radiation to reach the earth. Tropospheric pollution, on the other hand, is much more widespread.

18.2.1. Tropospheric Pollution

Tropospheric pollutants may be gaseous or particulate in nature. The following are the major gaseous and particulate pollutants.

1. ***Gaseous air pollutants***: Oxides of sulphur, nitrogen and carbon; hydrogen sulphide; hydrocarbons; ozone and other oxidants.
2. ***Particulate pollutants:*** Dust, fumes, mist, spray, smoke etc.

Gaseous Air Pollutants

(a) ***Oxides of Sulphur:*** These are probably the most harmful of the common gaseous pollutants. The combustion of any sulphur containing material results in the formation of sulphur dioxide (SO_2) and sulphur trioxide (SO_3). Sulphur dioxide is the major constituent (~97%) of the mixture.

Sulphur dioxide is the most widespread and serious air pollutant. It has been reported that at lower concentrations, sulphur dioxide causes temporary spasm of the smooth muscle of the bronchioles. Sulphur dioxide is also considered to cause cough, shortness of breath and spasm of the larynx*. Sulphur dioxide can cause acute irritation to the membranes of the eyes resulting in tears and redness. Moreover, it reacts in the atmosphere to form other undesirable compounds such as sulphuric acid. Sulphuric acid droplets attached to soot particles may pass through the nose and damage the lungs.

Although sulphur dioxide is an irritant to living tissues, it is less harmful than sulphur trioxide to which it is converted according to the reaction:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \qquad (18.1)$$

The uncatalyzed oxidation of SO_2 is slow, but polluted air often contains particulate matter that catalyzes the oxidation. The reaction can be promoted by the presence of NO_2 or H_2O_2. The SO_3 reacts with water in the air (or in the lungs) to form H_2SO_4.

(b) ***Oxides of Nitrogen*** : The main constituents of dry air at sea level are : nitrogen 78% and oxygen about 20% by volume. But these two gases do not react with each other at ambient temperature. It is only at high temperatures (>1210°C) that they combine to yield significant quantities of nitric oxide (NO). Such reactions are common in the internal combustion engines, and in the coal and oil burning furnaces. Nitric oxide itself is not considered to have a significant

* *The larynx, which is the upper most part of the windpipe, consists of vocal chords which help in the production of sound. The larynx is, therefore, also called voice box.*

adverse effect on human health, even at elevated concentrations. However, it is oxidised by oxygen, and even more rapidly by ozone, to nitrogen dioxide, which is extremely toxic to living tissue and harmful to paints, textiles, and metals.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \quad (18.2)$$

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \quad (18.3)$$

Eventually, NO_2 is oxidised to nitrate, NO_3^- ion, and washed into the soil, where it serves as a fertilizer. The oxides of nitrogen are the second most abundant atmospheric pollutants. The most harmful effect of nitrogen oxides in the atmosphere, as we shall study later, is in the production of **photochemical smog**.

(c) ***Oxides of Carbon***

(i) *Carbon Monoxide :* Carbon monoxide (CO), a lethal gas, is produced as a result of incomplete combustion of carbon. Its main unnatural source is the incomplete combustion of fossil fuels, and the largest portion comes from the exhausts of motor vehicles. The complete combustion of butane, for example, requires 6.5 moles of oxygen per mole of the hydrocarbon. If only 6.0 moles of oxygen are present, then 1 mole of CO and 3 moles of CO_2 are produced.

$$C_4H_{10}(g)+6.5O_2(g) \rightarrow 4CO_2(g)+5H_2O(l) \quad (18.4)$$

$$C_4H_{10}(g)+6O_2(g) \rightarrow 3CO_2(g)+CO(g)+5H_2O(l) \quad (18.5)$$

The operation of engines with a lean fuel mixture, that is, with less fuel and more air, reduces the emission of CO.

Carbon monoxide is poisonous because it binds to haemoglobin much more strongly (about 200 times) than oxygen. The presence of CO, therefore, reduces the amount of haemoglobin available in the blood for the transport of oxygen to the body cells and, therefore, with less O_2 levels, normal metabolism is impaired. Depending upon its concentration, CO in the blood can cause mental impairment, laboured respiration, muscular weakness, dizziness and even death. There is also a strong evidence which links cigarette smoking to reduced mental performance (taking tests, driving automobiles), and to heart disease.

(ii) *Carbon Dioxide* : Carbon dioxide (CO_2) is a natural constituent of the atmosphere and is vital to all forms of plant life. Normally, it forms about 0.03% by volume of the atmosphere. With the increased use of fossil fuels (coal, oil), a large amount of carbon dioxide gets released into the atmosphere. In a balanced ecosystem, the CO_2 additionally released into the atmosphere is removed regularly by the green plants (because they require CO_2 for photosynthesis and they, in turn, emit oxygen, thus maintaining the cycle). Forests on the earth account for about 70% of all photosynthesis occurring at any time but with the extent of deforestation that has taken place to date, there is an increased build-up of CO_2 in the atmosphere.

Carbon dioxide causes mild narcotic effects, stimulation of the respiratory centre and leads to asphyxiation. The increasing concentration of CO_2 also changes the climatic conditions, especially by raising the global temperature. This phenomenon is known as the **Greenhouse effect.**

Global Warming and Greenhouse Effect

Greenhouse effect is the phenomenon in which earth's atmosphere traps the heat from the sun and prevents it from escaping into the outer space. The greenhouse effect received its name because the earth's atmosphere acts much like the glass or plastic roof and walls of a greenhouse. Sunlight enters a greenhouse through the transparent glass or plastic panes and heats the plants but the heat emitted by the plants in the form of infrared radiation cannot pass through the glass or plastic panes. As a result, the inside temperature increases. Similarly, the earth's atmosphere allows most of the sunlight that falls on it to pass through and heat the surface. But the heat radiated by the heated surface cannot pass freely into space, because certain gases called **greenhouse gases** such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFCs) and water vapour in the atmosphere absorb it. Thus, they add to the heating of the atmosphere.

The concentration of water vapour in the

atmosphere has not changed appreciably in recent years. There has, however, been a marked increase in the levels of other greenhouse gases. Deforestation and the large scale burning of fossil fuels, have contributed to the steady rise in the atmospheric concentration of CO_2. If these trends continue in the future, there could be an increase in the average temperature of the atmosphere resulting in climatic changes. For example, there may be less rainfall in temperate zones and more rainfall in the drier areas of the world. The other severe outcome of the global warming would be a rise in sea level due to increased rate of melting of glaciers. It has been estimated that the sea level may rise by 0.5 m to 1.5 m in the next 50 to 100 years. Higher sea levels would increase the frequency and severity of floods, damage coastal areas, cause loss of soil replenishment and sea water intrusion into rivers and other aquatic systems near the ocean. Increased CO_2 levels in the atmosphere are also expected to cause plants, undergoing photosynthesis, to take up the gas at a greater rate, so that plants in warmer climates with adequate rainfall would grow faster. An increase in average global temperature is likely to increase the incidence of infectious diseases such as malaria, sleeping sickness, dengue and yellow fever.

Acid Rain: A Growing Problem

Rainwater normally has a pH of 5.6 due to the formation of H^+ ions from the reaction of rainwater with carbon dioxide present in the atmosphere. $H_2O(l)+CO_2(g) \rightarrow 2H^+(aq) + CO_3^{2-}(aq)$. When the pH of the rain drops below 5.6, it becomes acidic. Acid rain is caused by the presence of oxides of sulphur and nitrogen in the atmosphere. Oxides of sulphur are released into the environment largely because of fossil fuel combustion, ore smelting, petroleum refining and sulphur-based industries. Nitrogen oxides are emitted into the atmosphere mainly from automobile exhausts and fossil fuel combustion. SO_2 and NO_2 after oxidation and reaction with water are major contributors to acid rain.

$$2SO_2(g) + O_2(g)+2H_2O(l) \rightarrow 2H_2SO_4(aq) \quad (18.6)$$

and

$$4NO_2(g)+O_2(g)+2H_2O(l) \rightarrow 4HNO_3(aq) \quad (18.7)$$

Acid rain is toxic to vegetation and aquatic life. It damages buildings and statues, and dissolves **heavy metals** from soils, rocks and sediments. The heavy metal ions such as copper, lead, mercury and aluminium, leached from the soil enter well waters and produce a variety of toxic effects. Acid rain also corrodes water conduit pipes resulting in the leaching of heavy metals such as iron, lead and copper into the drinking water.

Taj Mahal and Acid Rain

The air in the city of Agra, where Taj Mahal is located, contains very high levels of sulphur and nitrogen oxides. The resulting acid rain reacts with marble ($CaCO_3$) of Taj Mahal ($CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$) causing pitting in this wonderful monument that has attracted people from around the world. As a result, the monument is being slowly eaten away and the marble is getting discoloured and lustureless. The Government of India announced an action plan in early 1995 to prevent the disfiguring of this historical landmark.

This plan aims at clearing the air in the ***'Taj Trapezium'*** *— an area that includes the towns of Agra, Firozabad, Mathura and Bharatpur. Under this plan more than 2000 polluting industries lying inside the trapezium would switch over to the use of natural gas or liquefied petroleum gas instead of coal or oil. A new natural gas pipeline would bring more than half a million cubic metres of natural gas a day to this area People living in the city will also be encouraged to use liquefied petroleum gas in place of coal, kerosene or firewood. Vehicles plying on highways in the vicinity of Taj would be encouraged to use low-sulphur content diesel.*

Particulates in Atmospheric Pollution

The black smoke released into the air by a diesel truck is often the most obvious form of pollution that we routinely encounter. This smoke is composed of particulate matter. Particulates are the tiny solid or liquid particles suspended in air. These particles are usually individually invisible to the naked eye. Collectively, however, small particles often form a haze that restricts visibility. Particulates in the atmosphere may be **viable** or **non-viable**. The **viable particulates** are the minute living organisms that are dispersed in atmosphere. These include bacteria, fungi, moulds, algae etc. It may be noted that human beings are allergic to some of the fungi found in air. Fungi can also cause plant diseases. **Non-viable particulates** of importance are formed either by the breakdown of larger materials or by the condensation of minute particles and droplets. There are four types of non-viable particulates in the atmosphere: **mists, smoke, fumes** and **dust**.

(a) ***Mists*** are produced by particles of spray liquids and the condensation of vapours in air. Examples are portions of herbicides and insecticides that miss their targets and travel through the air to form mists.

(b) ***Smoke*** denotes very small soot particles produced by burning and combustion of organic matter. Oil smoke, tobacco smoke and carbon smoke are typical examples of this type of particulate emission.

(c) ***Fumes*** are condensed vapours; fumes of metals are the well-known particulates of this type. Examples of this category also include metallurgical fumes and alkali fumes.

(d) ***Dust*** consists of fine particles produced during crushing, grinding and attribution of solid materials. Non- viable dust particulates in the atmosphere consist of ground limestone, sand tailings from flotation, pulverised coal, cement, fly ash and silica dust.

The effects of particulate pollutants are largely dependent on the particle size. Whereas the coarser particles of size greater than 5 microns are likely to lodge in the nasal passages, the smaller ones are more likely to penetrate into the lungs — the rate of penetration being inversely proportional to the size of particles. A number of these fine particulates are carcinogens. Inhalation of small particles irritates the lungs and exposure to such particles for long periods of time causes 'scarring' or 'fibrosis' of the lung lining. This type of disease is well known in industrial settings and is termed as "**Pneumoconiosis**".

The suspended particulate matter in the atmosphere effectively reduces the amount of light rays reaching the surface of the earth and thus lowers the temperature of the earth. By blocking the sunlight, they contribute to a drop in the earth's temperature and by providing condensation nuclei; they contribute to increased fog and rain in cities. Suspended particles in the city atmosphere also reduce the visibility. The visibility decreases as the atmospheric particulate concentrations increase.

Smogs

Smogs which describe the "smoke-fog" like conditions, are the best-known examples of air pollution that occurs in many cities throughout the world. There are two types of smogs: (i) classical smogs which occur in cool humid climate and are the result of buildup of sulphur oxides and particulate matter from fuel combustion and (ii) photochemical smogs which occur in warm, dry and sunny climate and result from the action of sunlight on the nitrogen oxides and hydrocarbons produced by automobiles and factories. Photochemical smog is an oxidising smog having a high concentration of oxidising agents whereas classical smog is chemically reducing smog with high concentrations of SO_2. Photochemical smog occurs generally in those cities which have very large populations and high vehicular density.

Formation of photochemical smog: The chemistry of formation of photochemical smog centres around nitric oxide (NO). At the high temperatures, in the petrol and diesel engines of cars and trucks, N_2 and O_2 react to form a small quantity of NO, which is emitted into the air with the exhaust gases. This NO is oxidised in air to NO_2 which in turn absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atom. (photochemical decomposition)

$$NO_2(g) \xrightarrow{h\nu} NO(g) + O(g) \qquad (18.8)$$

Oxygen atoms are very reactive and can combine with O_2 to form ozone:

$$O(g) + O_2(g) \rightarrow O_3(g) \quad (18.9)$$

The O_3 formed in the above reaction reacts rapidly with the NO(g) formed in reaction (18.8) to regenerate NO_2.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g) \quad (18.10)$$

Both NO_2 and O_3 are strong oxidising agents and can react with the unburnt hydrocarbons in the polluted air to produce chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN) that cause the eyes to water and burn and are harmful to the respiratory system. The brownish haze of photochemical smog is largely attributed to the brown colour of NO_2.

$$3CH_4 + 2O_3 \longrightarrow \underset{\text{Formaldehyde}}{3CH_2=O} + 3H_2O \quad (18.11)$$

Acrolein and peroxyacetyl nitrate (PAN) are particularly noxious.

$CH_2=CHCH=O$ — Acrolein

CH_3COONO_2 (O) — Peroxyacetyl nitrate (PAN)

Effects of Photochemical Smog

The three main components of photochemical smog are nitrogen oxides, ozone and organic derivatives (such as acrolein, formaldehyde, PAN etc.). Each contributes to the hazardous effects of smog. Pungent smelling, smog-produced ozone is known to be toxic. It can cause coughing, wheezing, bronchial constriction and irritation to the respiratory mucous system. Peroxyacyl nitrates and aldehydes found in smog are eye irritants. Materials are also adversely affected by some smog components. Rubber has a high affinity for ozone and is cracked and aged by it. Smog also affects plants in an adverse way. Ozone is also known to cause damage to vegetation and reduction in plant growth and crop productivity. Of all the components of smog, PAN has the highest toxicity to plants, attacking younger leaves and causing 'bronzing' and glazing' of their surfaces.

Control of Photochemical Smog

Efforts have been made to suppress or control formation of photochemical smog. Installation of efficient catalytic converters in the automobiles is the most straightforward way of reducing smog formation as it prevents the release of nitrogen oxides and hydrocarbons to the atmosphere. Photochemical smog can also be suppressed by certain compounds, which act as free radical traps. When these compounds are sprayed in the atmosphere, they generate free radicals which readily combine with free radical precursors of photochemical smog.

18.2.2. Stratospheric Pollution

Mechanism of Ozone Layer Depletion

Ozone (O_3), a light bluish gas found in the stratosphere, absorbs ultraviolet (UV) radiation of the sun which is harmful to the living things. O_3 therefore, acts as one of the earth's most important life support systems. In recent years, however, there have been reports of the depletion of this protective ozone layer. The effects of the depletion of ozone layer in the stratosphere include in increased human cataracts, skin cancer, reduction of planktons in ocean waters, depletion of plants and crops. The major cause of ozone layer destruction is believed to be the release of chlorofluorocarbon compounds (CFCs), also known as **freons,** into the atmosphere. These compounds are chemically unreactive, non-toxic and odourless. They are used as solvents, aerosol propellants, refrigerant fluids and blowing agents for plastic foams. These compounds persist in the atmosphere for years and eventually enter its upper layers where they get broken down by the powerful UV radiation emitted by the sun. The lifetime of CF_2Cl_2 (CFC-12) , for example, is 139 years while that for $CFCl_3$ (CFC-11) is about 77 years. The decomposition products of CFCs destroy ozone as is clear from the following reactions.

UV radiation causes the chlorofluorocarbon to dissociate:

$$CF_2Cl_2(g) + h\upsilon \rightarrow Cl\cdot(g) + \cdot CF_2Cl(g) \quad (18.12)$$

A highly reactive chlorine atom (free radical) is produced. This reacts with ozone to form chlorine monoxide:

$$Cl^-(g) + O_3(g) \rightarrow ClO\cdot(g) + O_2(g) \quad (18.13)$$

Reaction with atomic oxygen produces more chlorine atoms

$$ClO\cdot(g) + O(g) \rightarrow Cl\cdot(g) + O_2(g) \quad (18.14)$$

These chlorine atoms are free to react with more ozone (18.13). Many O_3 molecules can thus be destroyed for each chlorine atom produced. It has been shown that over one thousand ozone molecules can be destroyed by one Cl. Great loss of ozone has occurred since the early 1980s in the ozone layer over Antarctica producing a massive **ozone hole** which occurs mainly during

NOBEL PRIZE FOR OZONE LAYER RESEARCHERS

Paul Crutzen

Mario Molina

F. Sherwood Rowland

Three chemistry researchers were awarded the 1995 Nobel Prize in Chemistry for atmospheric studies which led to an understanding of how the ozone layer forms and decomposes. These researchers were ***Prof. Paul Crutzen*** of the Max-Plank Institute for Chemistry in Mainz, Germany, ***Prof. Mario Molina*** of the Department of Earth, Atmospheric and Planetary Sciences at Massachussetts Institute of Technology, USA and ***Prof. F. Sherwood Rowland*** of the Department of Chemistry at the University of California at Irvine in USA. These three winners of the Nobel Prize were the first ever to receive the award for atmospheric chemistry or environmental science.

spring time (September - October) and replenishes after spring (November-December). Scanty depletion of ozone is also known to occur over Arctic and over a few pockets in non-polar regions.

Ozone Depletion Over Antarctica

While the chain reactions (18.12 to 18.14) described above can theoretically occur all over the stratosphere, the depletion of ozone layer leading to ozone hole has, however, been mainly observed in the stratosphere over Antarctica. In other parts of the stratosphere, two alternative reactions shown below use chlorine monoxide and chlorine atoms.

$$ClO\cdot(g) + NO_2(g) \rightarrow ClONO_2(g) \qquad (18.15)$$

$$Cl\cdot(g) + CH_4(g) \rightarrow CH_3\cdot(g) + HCl(g) \qquad (18.16)$$

Oxides of nitrogen in the stratosphere scavenge the chlorine monoxide radicals. The presence of methane scavenges chlorine atoms. The chlorine nitrate formed in reaction (18.15) and hydrogen chloride formed in the reaction (18.16) thus act as natural sinks for reactive chlorine species. Once these are tied-up, the chain mechanism leading to ozone depletion is not initiated. Hence, no ozone hole is created.

In Antarctica, however, the conditions are quite different. During winters, special type of clouds, called **Polar Stratospheric Clouds** (PSCs) are formed over Antarctica. These clouds are of two types. **Type-I clouds**, which contain some solidified nitric acid trihydrate ($HNO_3 \cdot 3H_2O$), form at about - 77°C. **Type-II clouds**, which contain some ice, form at about -85°C. These clouds play an important role in ozone depletion.

On the surface of polar stratospheric clouds, chlorine nitrate, formed in reaction (18.15) undergoes two important transformations: i) it gets hydrolyzed,

$$ClONO_2(g)+H_2O(g) \rightarrow HOCl(g)+HNO_3(g) \qquad (18.17)$$

and ii) it reacts with hydrogen chloride formed in reaction (18.16).

$$ClONO_2(g) + HCl(g) \rightarrow Cl_2(g) + HNO_3(g) \qquad (18.18)$$

Reactions (18.17) and (18.18) convert important sinks of chlorine atoms into hypochlorous acid and molecular chlorine. Even under mild conditions, hypochlorous acid and molecular chlorine can be reconverted into reactive chlorine atoms, paving way for ozone depletion.

Ozone depletion over Antarctica occurs during

spring time (from early September to late October) and gets replenished after spring time. During the spring time sun begins to shine over Antarctic skies. HOCl and Cl_2 (reactions 18.17; 18.18) are photolyzed by sunlight.

$$HOCl\,(g) + h\upsilon \rightarrow \cdot OH\,(g) + Cl\cdot(g) \qquad (18.19)$$

$$Cl_2\,(g) + h\upsilon \rightarrow 2\,Cl\cdot(g) \qquad (18.20)$$

The reactive chlorine atoms thus formed are rendered free to deplete ozone through the chain mechanism reactions (18.13) and (18.14).

During winters when PSCs are formed over Antarctica, stable wind patterns in the stratosphere called the **Polar Vortex** encircle the continent. Polar Vortex is a tight whirlpool of winds. It is so rigid that air within it is isolated from the sun and from the warmer air of the temperate region. Thus, as long as polar vortex surrounds Antarctica, the ozone rich air from the non-polar region is prevented from 'filling up' the ozone hole. Polar vortex remains intact throughout the Antarctic spring. After the spring, the intensity of sunlight increases and the vortex breaks down (sometime in November), and the ozone rich air from the temperate region rushes in and replenishes the ozone hole.

18.3. WATER POLLUTION

The quality of drinking water is very important for human welfare. The pollution of water by sewage has been linked to the spread of diseases such as cholera and typhoid fever. Table 18.3 lists the major water pollutants and their sources.

In addition, industrial wastes also contaminate water.

(i) ***Heavy Metals :*** Metals such as Cd, Pb and Hg may be present in industrial or mining waste. These metals can prove poisonous to humans — Cadmium and mercury can cause kidney damage, and lead poisoning can cause damage to the kidneys, liver, brain and central nervous system. All of these metals are cumulative poisons — the body does not excrete them and their concentration builds up.

(ii) ***Detergents and Fertilizers :*** These may contain phosphates as additives. The addition of phosphorus to water, in the form of the phosphate anion PO_4^{3-}, encourages the formation of algae, which reduces the dissolved oxygen concentration of water. This process, known as **eutrophication,** impedes the development of higher life forms, such as fish.

(iii) ***Acid-polluted Water (pH<3) :*** This is deadly to most forms of aquatic life. Water downstream from a mine may be contaminated by acid mine drainage, the result of microbial oxidation of discarded waste material at the mine site. Acid mine water principally contains sulphuric acid produced by the oxidation of iron pyrites (FeS_2). Industrial wastes and acid rain may also contribute to the acidity of natural waters.

Table 18.1 Major Water Pollutants

Pollutant	Source
Microorganisms	Domestic sewage
Organic wastes	Domestic sewage, animal waste, decaying animals and plants and discharge from food processing factories
Plant nutrients	Chemical fertilizers
Toxic heavy metals	Industries and chemical factories
Sediments	Erosion of soil by agriculture and strip mining
Pesticides	Chemicals used for killing insects, fungi and weeds
Radioactive substances	Mining of uranium containing minerals
Heat	Cooling water used by industrial plants (which is discharged as hot water)

(iv) ***Polychlorinated biphenyls (PCBs) :*** These chemicals are relatively recent additions to the list of contaminants of water. Having high stabilities, PCBs find many applications, for example they are used as fluids in transformers and capacitors. PCBs are resistant to oxidation and their release into the environment causes skin disorders in humans. They are reported to be carcinogenic.

18.3.1 International Standards for Drinking Water

The quality of water is of vital concern for mankind since it is directly linked with human welfare. There are some international standards for drinking water, which must always be obeyed if water is to be used for drinking purposes. These are:

Fluoride : Soluble fluoride is often added to drinking water to bring it up to a concentration of 1 ppm or 1 mg dm^{-3}. This concentration is within agreed safety limits and has been shown to protect teeth against decay. High concentrations of fluoride are poisonous and are harmful to bones and teeth at levels over 10 ppm (mg dm^{-3}).

Lead : The limit for the concentration of lead ions in drinking water is 50 ppb (μg dm^{-3}). If water is relatively acidic and lead pipes are used for water transport, then the water is liable to get contaminated with lead.

pH : The pH of drinking water should be between 5.5 and 9.5. A decrease in the pH of the water increases the solubility of metal ions.

Other Metals : The maximum recommended levels of common metals in drinking water are as follows.

Metal	Max. Concentration (ppm or mg dm^{-3})
Zn	5
Fe	0.2
Mn	0.05
Cu	3
Cd	0.005
Al	0.2

Sulphate : Sulphate is harmless at moderate levels, but excessive sulphate (>500 ppm) is thought to have a laxative effect.

Nitrate : Excess nitrate in drinking water can lead to *methemoglobinemia* ('blue-baby' syndrome). It also may be linked to stomach cancer, although this link has not been proved. A maximum limit of 50 ppm for the nitrate ion in drinking water has been set.

18.3.2 Importance of Dissolved Oxygen in Water

The concentration of dissolved oxygen in water is of vital importance for the support of aquatic life. The fish growth is inhibited if the dissolved concentration of oxygen in water is below 6 ppm. The lower the concentration of dissolved oxygen, the more polluted is the water sample. Oxygen reaches water through two sources. The first is that oxygen dissolves at the surface of the water from the atmosphere. Still water takes up oxygen slowly whereas turbulent water takes it up more rapidly since bubbles are often submerged. The second source of oxygen in water is from photosynthesis. Where there are many aquatic green plants present, the water often becomes supersaturated with oxygen during the hours of daylight. However, after dark, photosynthesis stops but the plants continue to respire and actually reduce the amount of dissolved oxygen. Therefore, during a 24 hour period, some water samples have a considerable range of dissolved oxygen levels.

Various processes contribute to the deoxygenation of water. The dissolved oxygen in water is consumed rapidly by microorganisms to oxidise organic matter of sewage.

$$[CH_2O](aq) + O_2(aq) \xrightarrow{\text{Microorganisms}} CO_2(aq) + H_2O(l)$$

Unless the water restores its dissolved oxygen concentration for example, by the turbulent flow of shallow waters or by a reaction, it is not able to support many organisms.

In addition to the microorganism — mediated oxidation of organic matter described above, oxygen in water may be consumed by the bio-oxidation of the nitrogenous material.

$$NH_4^+(aq) + 2O_2(aq) \longrightarrow 2H^+(aq) + NO_3^-(aq) + H_2O(l)$$

and by the chemical or biochemical oxidation of chemical reducing agents:

$$4Fe^{2+}(aq) + O_2(aq) + 10H_2O(l) \rightarrow 4Fe(OH)_3(s) + 8H^+(aq)$$

$$2SO_3^{2-}(aq) + O_2(aq) \rightarrow 2SO_4^{2-}(aq)$$

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)

The polluted water may contain large amounts of inorganic and organic compounds. Some of these can be oxidised by dissolved oxygen in the presence of microorganisms. **Biochemical oxygen demand (BOD)** is a measure of the dissolved oxygen that would be needed by the microorganisms to oxidise these compounds. BOD, therefore, is a measure of the contamination caused by the totality of those compounds which can be oxidised in the presence of microorganisms. A large number of organic and inorganic compounds, however, are resistant to microbial oxidation. They, therefore, don't contribute to the BOD, though their presence makes water unfit for consumption. The BOD is taken as a realistic measure of water quality — 'clean water' would have a BOD value of less than 5 ppm whereas highly polluted river water could have a BOD value of 17 ppm or more. In order to find out BOD, the water sample is first saturated with oxygen. It is then incubated at constant temperature, usually 20°C, for five days. This allows time for microorganisms in the water sample to oxidise pollutants. The remaining amount of dissolved oxygen is determined and BOD is obtained by subtraction. BOD measurement takes a few days (generally five days), so another parameter called the **chemical oxygen demand (COD)** is sometimes measured.

In a COD determination, the water sample is treated with a known quantity of an oxidising agent, usually potassium dichromate $K_2Cr_2O_7$ in acidic medium.. This reagent oxidises most of the polluting substances, including those which are resistant to microbial oxidation. The remaining $K_2Cr_2O_7$ is determined by back titration with a suitable reducing agent like Mohr's salt. From the concentration of $K_2Cr_2O_7$ consumed, the amount of oxygen used in the oxidation may be calculated using the following chemical equation

$$K_2Cr_2O_7\,(aq) + 4\,H_2SO_4\,(aq) \rightarrow K_2SO_4\,(aq) + Cr_2(SO_4)_3\,(aq) + 4H_2O(l) + 3O(aq)$$

The results are expressed in terms of amount of oxygen, in ppm, that would be required to oxidise the contaminants. This is called COD.

18.4 LAND POLLUTION

Most of the land pollution is caused by pesticides and other chemicals which are added to the soil to grow better crops. Often, a pesticide poisons many more organisms than those intended. Some of these poisons pass through food chains and eventually reach harmful proportions. Solid wastes are another cause of land pollution.

18.4.1 Pesticides

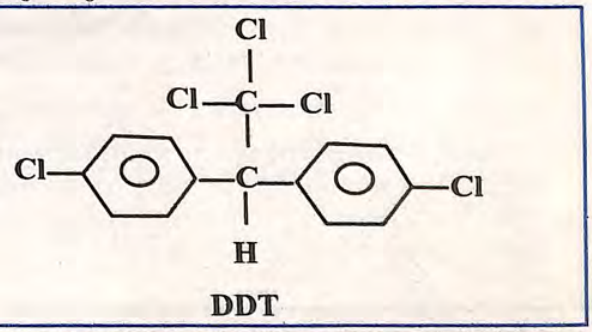
Pesticides are substances that are used to kill or block the reproductive processes of unwanted organisms. Synthetic pesticides are of concern to us, because of the possible effect upon human health through eating of food, or drinking water, contaminated with these chemicals. Most pesticides can be put into one of three categories:

(i) Insecticides

Control of insects by insecticides helps to curb disease (for example malaria and yellow fever) and protect crops. Organochlorines are a group of compounds which have been developed and used as insecticides since the 1950s. The best-known organochlorine compound is DDT* (dichlorodiphenyltrichloroethane). Organochlorines are stable in the environment, toxic to insects in small amounts, but much less so to humans; and, because they are organic compounds, not very soluble in water. The advantage of these insecticides is that, being persistent, they show their biological activity for long periods of time. On the negative side, these insecticides by accumulating in the environment affect many non-target organisms, not just the target pests. It is primarily because of their persistent nature that many of these insecticides have been phased out of use.

(ii) Herbicides

Herbicides are used to kill weeds. Sodium chlorate, $NaClO_3$ and sodium arsenite Na_3AsO_3 were commonly used as weed killers



DDT

* 2,2-bis (p-chlorophenyl)-1,1,1- trichloroethane

in the first half of the last century, but inorganic arsenic compounds, in particular, are toxic to mammals. Organic herbicides are, therefore, now used. They are much more toxic to certain types of plants than to others. Organic herbicides such as triazines are pesently widely used to kill weeds in cornfields.

(iii) Fungicides

Fungicides are used to check the growth of fungi. Fungi, as you know, are the plants without chlorophyll. They, therefore cannot use solar energy to convert carbon dioxide and water into energy-rich carbohydrates. They live as saprophytes on decaying organic matter or as parasites at the expense of living organisms. Hence they are deemed as a threat to human interests. Fungicides are important because they counter the growth of fungi. Organic compounds of mercury have been used as fungicides. These compounds break down in soil and this has had disastrous consequences-many human deaths in Iraq (1971-1972) resulted from the people eating bread made from grain that had been treated with the fungicide methylmercury.

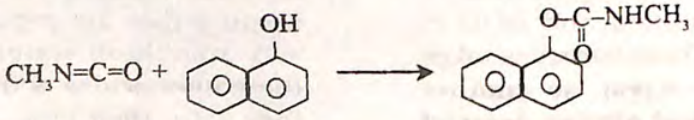
Bhopal Gas Tragedy

A major gas tragedy took place on the night of December 2, 1984, when a dense cloud of deadly methyl isocyanate (MIC) gas leaked from a storage tank of the Union Carbide Ltd. plant in Bhopal.

Methyl isocyanate was used to manufacture the insecticide carbaryl, marketed under the commercial name, sevin in this plant. Methyl isocyanate was prepared by the reaction of methylamine, CH_3NH_2 with phosgene, $COCl_2$.

$$CH_3NH_2 + COCl_2 \rightarrow \underset{\text{MIC}}{CH_3N=C=O} + 2HCl$$

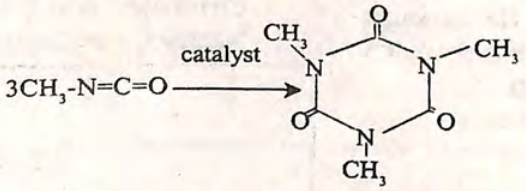
and stored in abundance. Subsequently it was treated with l-napthol to produce carbaryl



There were three tanks in the plant that stored methyl isocyanate. Pressure rose in one of the tanks and blasted its release valve thereby letting methyl isocyanate escape into the atmosphere. What caused the escape of methyl isocyanate gas? A plausible explanation is that possibly a small amount of water seeped into the storage tank and initiated the following hydrolysis reaction

$$CH_3N=C=O + H_2O \longrightarrow CH_3NH_2 + CO_2$$

Further the water that entered the tank was not pure and the impurities present initiated the following polymerisation reaction



Thus it was perhaps the simultaneous occurrence of the above two exothermic reactions that led to the escape of extrermely toxic methyl isocyanate gas from the reservoir.

As the cloud of methyl isocyanate rose over the city, it caused immense loss of life and injury to people and live stock.

18.5 STRATEGY FOR CONTROL OF ENVIRONMENTAL POLLUTION

18.5.1 The Management of Waste

The production and improper disposal of waste are causes for a great deal of environmental pollution. In addition to the household waste, which includes sewage and municipal garbage, many toxic industrial wastes from manufacturing processes require treatment and/or safe disposal.

Recycling

When materials are recycled, there are several benefits, apart from saving on the cost of raw materials, waste disposal costs are reduced. Examples of recycling by industry are:

1. the collection and recycling of glass (in bottle banks);
2. the use of scrap metal in the manufacture of steel;
3. the recovery of energy from burning combustible waste.

Thus recycling converts waste into wealth.

Sewage treatment

The main stages in the treatment of sewage are as follows:

1. The removal of large solids that get into the system by filtering the waste water through screens. The solids that are removed are disposed of in landfill sites.
2. Settlement in tanks to allow the removal of solids that settle out (called **sludge).** This process also allows removal of grease, which floats to the surface and can be skimmed off.
3. The degradation of the organic content of waste water by microbial oxidation.
4. Application of various physical and chemical processes for improving the quality of waste water. The processes include chemical removal of phosphate, coagulation, filtration and disinfection using chlorine.

The safe disposal of the sludge produced during water treatment is a problem.

The sludge is dried and then may be *incinerated, digested or dumped.*

Incineration

Incineration converts organic materials to CO_2 and H_2O. It may serve to destroy household waste, chemical waste and biological waste (e.g. from hospitals). A high temperature is required, usually in excess of 1000°C, and a plentiful supply of oxygen. Exhaust gases must be filtered. The process greatly reduces the volume of waste - an inorganic ash is left behind, which is disposed of as landfill. Incineration provides a means to dispose of the relatively inert PCBs, and the high temperatures generated allow endothermic reactions, such as the destruction of C-Cl bonds in organochlorine compounds, to take place. The chief disadvantage of incineration is that it leads to air pollution. Further the ash from municipal incinerators is very finely divided and can be ingested into the lungs. Incomplete combustion of PCBs can cause formation of highly toxic chloro compounds such as polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs). This is most likely to happen in older municipal waste incinerators.

Digestion

Anaerobic digestion occurs when microorganisms degrade wastes in the absence of oxygen. It may be used to treat sewage sludge, but the process can also be used to degrade a variety of toxic organic wastes. Carbon dioxide and methane, which may be used as a fuel, are the products. The overall process is the conversion of the organic material into carbon dioxide and methane i.e.

$$2\{CH_2O\} \longrightarrow CO_2\,(g) + CH_4(g)$$

Dumping

Ocean dumping of sewage sludge has been widely practiced in the seas around the world. However, the practice of application of sludge to the land is increasing. The sludge contains nitrogen and phosphorus which make it useful as a fertilizer. Urban areas produce sludge with high toxic metal content, so the amount of such sludge dumped in this way must be carefully controlled.

18.5.2 Green Chemistry : A New Route to Protection of Environment

Green Chemistry or environmentally benign chemistry, introduced in 1990s, focuses on processes and products that reduce or eliminate the use and generation of hazardous substances. For success in achieving the objectives of green chemistry, one has to take care of many aspects. The use of starting materials — reagents and solvents that pose less hazard to man and his environment, is one aspect. Using raw materials

more efficiently and generating less waste is another. In this regard, the utilisation of reactions that are simple additions which completely incorporate the starting materials into the final product and, therefore, do not produce waste that needs to be treated, disposed of, or otherwise dealt with, becomes a goal.

Green chemistry and the design and development of green chemical products and processes follow the same tradition of scientific discovery and understanding that has characterized chemistry from its origins. Green chemistry simply utilises the information that is now available to the scientific community about the toxicity and other hazards posed by certain chemicals in order to fully evaluate the negative as well as positive impact of the chemistry being designed. Databases of information on the hazardous properties of chemicals have only recently become available. In the previous years the absence of these data meant that chemists could not effectively evaluate the consequences of the chemical substances that were being designed and synthesized. Since this is no longer the case, it is the responsibility of the chemists and chemical community to use this information.

Achievements of Green Chemistry

Since the inception of green chemistry, chemists from all over the world are using their creative and innovative skills to develop new processes, synthetic methods, analytical tools, reaction conditions, catalysts, etc.. A lot of success has been achieved on this front. The processes developed include among others

(i) Development of a new method of synthesizing ibuprofen in 99% yield, avoiding the usage of large quantities of solvents and wastes associated with the traditional stoichiometric use of auxiliary chemicals when effecting chemical coversions.

(ii) Development of a method for 'catalytic dehydrogenation of diethanolamine' in which a new technique allows the production of an environmentally friendly herbicide in a less dangerous way. This technology represents a major breakthrough because it avoids the use of cyanide and formaldehyde. It is safer to operate, produces high overall yield and has fewer process steps.

(iii) Development of processes using carbon dioxide as the blowing agent, for manufacture of polystyrene foam sheet packaging material. This techlology allows elimination of chlorofluorocarbon blowing agents, chemicals that contribute to ozone depletion, global warming and ground level smog.

(iv) Designing of a safer marine antifouling compound 'Sea-nine' that degrades far more rapidly than organotins which persist in the marine environment and cause pollution problems.

SUMMARY

Our environment contains many chemical species, some of these occur naturally while others are produced as a result of certain human activities. Environmental chemistry is the study of the origin, transport, reactions, effects and fates of these chemical species. Some of the chemical species released into the environment are harmful and pollute the atmosphere, water and land. Tropospheric pollution is mainly due to gaseous pollutants and particulate pollutants. Important gaseous pollutants include oxides of sulphur, carbon and nitrogen, hydrogen sulphide, hydrocarbons and ozone while dust, fumes, spray and smoke etc. constitute the particulate pollutants. Increasing concentration of gaseous pollutants such as CO_2 is also the cause of greenhouse effect which causes global warming and climatic changes. Oxides of carbon, nitrogen and sulphur, besides causing air pollution, are also responsible for acid rain. Acid rain is harmful for vegetation, aquatic life, statues, buildings etc. The presence of atmospheric pollutants also leads to the important environmental phenomenon of formation of smogs. Depletion of ozone layer in the stratosphere leading to harmful UV radiation on earth is the result of stratospheric pollution. The presence of chlorofluorocarbon compounds (CFCs) in the stratosphere is responsible for this depletion. These compounds get broken down by the UV radiation emitted by the sun and the resulting decomposition products react with O_3 leading to its depletion. The formation of ozone hole resulting from the depletion of ozone layer over Antarctica during spring time and its replenishment after spring can be explained in the light of formation of polar stratospheric clouds and polar vortex.

The quality of water is of vital concern for the mankind. Water, in order to be fit for drinking purpose, must conform to international standards set up in this regard. Water can get polluted by various contaminants. The pollution of water also affects the amount of oxygen in it. Dissolved oxygen in water plays a very important role in the support of aquatic life. Oxygen dissolves in water through two sources; atmosphere and photosynthesis. Different water samples differ in their content of dissolved oxygen. The lower the concentration of oxygen in a sample of water, the more polluted the water sample is. Deoxygenation of water takes place through oxidation of organic matter, nitrogeneous matter and other chemical reducing agents present in water.

Pesticides, the chemicals added to the soil to grow better crops and solid wastes are generally the cause of the land pollution. Various steps are needed for the control of environmental pollution. Among these, the management of waste is of great importance. Important steps in the management of waste include recycling, sewage treatment, sludge treatment-incineration, digestion and dumping. A recent attempt at the prevention of environmental pollution is the introduction of Green Chemistry. This new branch of chemistry deals with processes and products that reduce or eliminate the use and generation of hazardous substances.

EXERCISES

18.1 What is environmental chemistry? Discuss its social relevance.

18.2 Define an environmental pollutant. What do you understand by an environmental pollution model?

18.3. Why does the rain water normally have a pH of about 5.6? When does it become acid rain?

18.4 What is the cause of acid rain? How is it harmful to the environment?

18.5 Why is acid rain considered a threat to Taj Mahal?

18.6 Explain giving reasons "The presence of CO reduces the amount of haemoglobin available in the blood for carrying oxygen to the body cells".

18.7 What do you understand by Greenhouse effect? What are the major Greenhouse gases?

18.8 Why does Greenhouse effect lead to the global warming? What could be the consequences of global warming ?

18.9 What do you understand by (i) Mists; (ii) Smoke; (iii) Fumes and (iv) Dust?

18.10 What is Pneumoconiosis? How does it occur?

18.11 What are smogs? Distinguish between classical and photochemical smogs.

18.12 How is photochemical smog formed? What are its effects? How can it be controlled?

18.13 State briefly the reactions causing ozone layer depletion in the stratosphere.

18.14 What do you understand by ozone hole? Why does it occur mainly over Antarctica?

18.15 The depletion of ozone layer occurs over Antarctica during spring time and it gets replenished after spring time. Explain.

18.16 What do you understand by (i) polar stratospheric clouds; (ii) polar vortex.

18.17 Fish do not always grow as well in warm as in cold water. Why?

18.18 List five major water pollutants giving their sources.

18.19 What do you understand by the term eutrophication? How does it threaten the development of fish?

18.20 Discuss the importance of dissolved oxygen in water. What processes are generally responsible for the deoxygenation of water?

18.21 How does oxygen reach water? How is the oxygen content of a sample of water measured?

18.22 What do you understand by BOD and COD? How are these determined?

18.23 Write a short note on Bhopal Gas Tragedy.

18.24 Explain, giving reactions, the plausible explanation for the escape of methyl isocyanate gas from the Union Carbide Ltd. Plant, in Bhopal on Dec. 2, 1984.

18.25 "Oxygen plays a key role in the troposphere while ozone, in the stratosphere" Elucidate.

Definitions of the SI Base Units

Metre (m): The metre is the length of path travelled by light in vacuum during a time interval of 1/299 792 458 of a second (17th CGPM, 1983).

Kilogram (kg): The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram (3rd CGPM, 1901).

Second (s): The second is the duration of 9192631770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom (13th CGPM, 1967).

Ampere (A): The ampere is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} Newton per metre of length (9th CGPM, 1948).

Kelvin (K): The kelvin, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water (13th CGPM, 1967).

Mole (mol): The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles (14th CGPM, 1971).

Candela (cd): The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of (1/683) watt per steradian (16th CGPM, 1979).

(The symbols listed here are internationally agreed and should not be changed in other languages or scripts).

Elements, their Atomic Number and Molar Mass

Element	Symbol	Atomic Number	Molar mass/ g mol^{-1}
Actinium	Ac	89	227.03
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.91
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251.08
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	247.07
Dubnium	Db	105	(263)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(252)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257.10)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	(269)
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	(262.1)
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.96
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitnelum	Mt	109	(268)
Mendelevium	Md	101	258.10

Element	Symbol	Atomic Number	Molar mass/ g mol^{-1}
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	210
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.04
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(266)
Selenium	Se	34	78.96
Silicon	Si	14	28.08
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	(98.91)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Ununbium	Uub	112	(277)
Ununnilium	Uun	110	(269)
Unununium	Uuu	111	(272)
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

The value given in parenthesis is the molar mass of the isotope of largest known half-life.

APPENDIX III

A. Specific and Molar Heat Capacities for Some Substances at 298 K and one Atmospheric Pressure

Substance	Specific Heat Capacity (J/g)	Molar Heat Capacity (J/mol)
air	0.720	20.8
water (liquid)	4.184	75.4
ammonia (gas)	2.06	35.1
hydrogen chloride	0.797	29.1
hydrogen bromide	0.360	29.1
ammonia (liquid)	4.70	79.9
ethyl alcohol (liquid)	2.46	113.16
ethylene glycol (liquid)	2.42	152.52
water (solid)	2.06	37.08
carbon tetrachloride (liquid)	0.861	132.59
chlorofluorocarbon (CCl_2F_2)	0.5980	72.35
ozone	0.817	39.2
neon	1.03	20.7
chlorine	0.477	33.8
bromine	0.473	75.6
iron	0.460	25.1
copper	0.385	24.7
aluminium	0.902	24.35
gold	0.128	25.2
graphite	0.720	8.65

B. Molar Heat Capacities for Some Gases (J/mol)

Gas	C_p	C_v	$C_p - C_v$	C_p / C_v
Monatomic*				
helium	20.9	12.8	8.28	1.63
argon	20.8	12.5	8.33	1.66
iodine	20.9	12.6	8.37	1.66
mercury	20.8	12.5	8.33	1.66
Diatomic†				
hydrogen	28.6	20.2	8.33	1.41
oxygen	29.1	20.8	8.33	1.39
nitrogen	29.0	20.7	8.30	1.40
hydrogen chloride	29.6	21.0	8.60	1.39
carbon monoxide	29.0	21.0	8.00	1.41
Triatomic†				
nitrous oxide	39.0	30.5	8.50	1.28
carbon dioxide	37.5	29.0	8.50	1.29
Polyatomic†				
ethane	53.2	44.6	8.60	1.19

*Translational kinetic energy only.
†Translational, vibrational and rotational energy.

Enthalpy of Combustion (at 298 K)

Substance	Enthalpy of Combustion, $\Delta_c H^\ominus$/kJmol^{-1}
Hydrocarbons	
CH_4(g), methane	-890
C_2H_2(g), ethyne (acetylene)	-1300
C_2H_4(g),ethane (ethylene)	-1411
C_2H_6 (g), ethane	-1560
C_3H_6 (g), propene(propylene)	-2058
C_3H_6 (g), cyclopropane	-2091
C_3H_8(g), propane	-2220
C_4H_{10}(g), butane	-2878
C_5H_{12}(g), pentane	-3537
C_6H_6(l), benzene	-3268
C_6H_6(g)	-3302
C_7H_8(l), toluene	-3910
C_7H_8 (g)	-3953
C_6H_{12} (l), Cyclohexane	-3920
C_6H_{12}(g)	-3953
C_8H_{18}(l), octane	-5471
Alcohols and phenols	
CH_3OH(l), methanol	-726
CH_3OH(g)	-764
C_2H_5OH(l), ethanol	-1368
C_2H_5OH(g)	-1409
C_6H_5OH(s), phenol	-3054
Carboxylic acids	
HCOOH(l), formic acid	-255
CH_3COOH(l), acetic acid	-875
$(COOH)_2$(s), oxalic acid	-254
C_6H_5COOH(s), benzoic acid	-3227
Aldehydes and ketones	
HCHO(g), methanal (formaldehyde)	-571
CH_3CHO(l), ethanal (acetaldehyde)	-1166
CH_3CHO(g)	-1192
CH_3COCH_3(l), propanal (acetone)	-1790
Sugars	
$C_6H_{12}O_6$(s), glucose	-2808
$C_6H_{12}O_6$(s), fructose	-2810
$C_{12}H_{22}O_{11}$(s), sucrose	-5645
Nitrogen Compounds	
$CO(NH_2)_2$(s), urea	-632
$C_6H_5NH_2$(l), aniline	-3393
NH_2CH_2COOH(s), glycine	-969
CH_3NH_2(g), methylamine	-1085

APPENDIX V

Physical Constants

Quantity	Symbol	Traditional Units	SI Units
Acceleration of gravity	g	980.6 cm/s	9.806 m/s
Atomic mass unit (1/12 the mass of ^{12}C atom)	amu or u	1.6606×10^{-24} g	1.6606×10^{-27} kg
Avogadro constant	N_A	6.022×10^{23} particles/mol	6.022×10^{23} particles/mol
Bohr radius	a_o	0.52918 Å 5.2918×10^{-9} cm	5.2918×10^{-11} m
Boltzmann constant	k	1.3807×10^{-16} erg/K	1.3807×10^{-23} J/K
Charge-to-mass ratio of electron	e/m	1.7588×10^{8} coulomb/g	1.7588×10^{11} C/kg
Electronic charge	e	1.60219×10^{-19} coulomb 4.8033×10^{-19} esu	1.60219×10^{-19} C
Electron rest mass	m_e	9.10952×10^{-28} g 0.00054859 u	9.10952×10^{-31} kg
Faraday constant	F	96,487 coulombs/eq 23.06 kcal/volt. eq	96,487 C/mol e^- 96,487 J/V.mol e^-
Gas constant	R	$0.8206 \frac{\text{L atm}}{\text{mol K}}$ $1.987 \frac{\text{cal}}{\text{mol K}}$	$8.3145 \frac{\text{kPa dm}^3}{\text{mol K}}$ 8.3145 J/mol.K
Molar volume (STP)	V_m	22.414 L/mol	22.414×10^{-3} m^3/mol 22.414 dm^3/mol
Neutron rest mass	m_n	1.67495×10^{-24} g 1.008665 u	1.67495×10^{-27} kg
Planck constant	h	6.6262×10^{-27} ergs	6.6262×10^{-34} J s
Proton rest mass	m_p	1.6726×10^{-24} g 1.007277 u	1.6726×10^{-27} kg
Rydberg constant	R_∞	3.289×10^{15} cycles/s 2.1799×10^{-11} erg	1.0974×10^{7} m^{-1} 2.1799×10^{-18} J
Speed of light (in a vacuum)	c	2.9979×10^{10} cm/s (186,281 miles/second)	2.9979×10^{8} m/s

$\pi = 3.1416$

$e = 2.71828$

$\ln X = 2.303 \log X$

$2.303\ R = 4.576$ cal/mol K $= 19.15$ J/mol K

$2.303\ RT$ (at 25°C) $= 1364$ cal/mol $= 5709$ J/mol

Some Useful Conversion Factors

Common Unit of Mass and Weight
1 pound = 453.59 grams

1 pound = 453.59 grams = 0.45359 kilogram
1 kilogram = 1000 grams = 2.205 pounds
1 gram = 10 decigrams = 100 centrigrams
= 1000 milligrams
1 gram = 6.022×10^{23} atomic mass units or u
1 atomic mass unit = 1.6606×10^{-24} gram
1 metric tonne = 1000 kilograms
= 2205 pounds

Common Unit of Volume
1 quart = 0.9463 litre
1 litre = 1.056 quarts

1 litre = 1 cubic decimetre = 1000 cubic centimetres = 0.001 cubic metre
1 millilitre = 1 cubic centimetre = 0.001 litre
= 1.056×10^{-3} quart
1 cubic foot = 28.316 litres = 29.902 quarts
= 7.475 gallons

Common Units of Energy
1 joule = 1×10^7 ergs

1 thermochemical calorie**
= 4.184 joules
= 4.184×10^7 ergs
= 4.129×10^{-2} litre-atmospheres
= 2.612×10^{19} electron volts
1 ergs = 1×10^{-7} joule = 2.3901×10^{-8} calorie
1 electron volt = 1.6022×10^{-19} joule
= 1.6022×10^{-12} erg
= 96.487 kJ/mol†
1 litre-atmosphere = 24.217 calories
= 101.32 joules
= 1.0132×10^9 ergs
1 British thermal unit = 1055.06 joules
= 1.05506×10^{10} ergs
= 252.2 calories

Common Units of Length
1 inch = 2.54 centimetres (exactly)

1 mile = 5280 feet = 1.609 kilometres
1 yard = 36 inches = 0.9144 metre
1 metre = 100 centimetres = 39.37 inches
= 3.281 feet
= 1.094 yards
1 kilometre = 1000 metres = 1094 yards
= 0.6215 mile
1 Angstrom = 1.0×10^{-8} centimetre
= 0.10 nanometre
= 1.0×10^{-10} metre
= 3.937×10^{-9} inch

Common Units of Force* and Pressure

1 atmosphere = 760 millimetres of mercury
= 1.013×10^5 pascals
= 14.70 pounds per square inch
1 bar = 10^5 pascals
1 torr = 1 millimetre of mercury
1 pascal = 1 kg/m.s^2 = 1 N/m^2

Temperature
SI Base Unit: Kelvin (K)

0 K = -273.15^{0}C
? K = ^{0}C + 273.15^0
?^{0}F = 1.8(^{0}C) + 32^0

$$?^0C = \frac{^0F - 32^0}{1.8}$$

---

* Force: 1 newton (N) = 1 kg.m/s^2, i.e.,the force that, when applied for 1 second, gives a 1-kilogram mass a velocity of 1 metre per second.

** The amount of heat required to raise the temperature of one gram of water from 14.5^{0}C to 15.5^{0}C.

† Note that the other units are per particle and must be multiplied by 6.022×10^{23} to be strictly comparable.

Answer to Some Selected Problems

UNIT 1

1.3 7.10×10^{-3} kg

1.4 (a) 2.5×10^{-2} m^3 (b) 2.5×10^{3} mg dL^{-1} (c) 1.54×10^{3} pm μs^{-1}
(d) 2.66×10^{-6} $\mu g\ \mu m^{-3}$ (e) 3.2×10^{-4} mL s^{-2}

1.15 39.948 g/mol

1.16 (b) 3.3 g

1.18 (i) 3.131×10^{25} atoms (ii) 13 atoms (iii) 7.8286×10^{24} atoms

1.19 8.03×10^{-2} mol

1.21 1.33×10^{21} magnesium atoms

1.24 0.089 M $NaNO_3$

1.25 30.7 mL of NaOH

1.26 0.26 mol, and HCl is limiting reagent

1.28 Fe = 27.93%, S = 24.05%, O = 48.01%

1.29 Empirical formula CH, molar mass = 26.0 g mol^{-1}, molecular formula C_2H_2

1.30 0.94 g $CaCO_3$

1.31 8.40 g HCl

1.32 Mass of NaCl = 23.4 g, 250 ml

UNIT 2

2.1 2.5 bar

2.2 0.8 bar

2.4 70 g/mol

2.5 $M_B = 4M_A$

2.6 202.5 mL

2.7 8.314×10^{4} Pa

2.8 1.8 bar

2.9 $3g/dm^3$

2.10 1247.7 g

2.11 3/5

2.12 50 K

2.13 4.2154×10^{23} electrons

2.14 1.90956×10^{6} year

2.15 56.025 bar

2.16 37 98 kg

2.17 5.05 L

2.18 40 g mol^{-1}

2.19 81.12 cm from HCl end

2.20 417.4 g mol^{-1}

2.21 20 g mol^{-1}

2.22 7382.6 J
2.23 0.8 bar
2.29 1.347 bar

UNIT 3

3.1 (i) 1.099×10^{27} electrons (ii) 5.48×10^{-7} kg, 9.65×10^{4}C
3.2 (i) 6.022×10^{24}electrons
(ii) (a) 2.4088×10^{21} neutrons (b) 4.0347×10^{-6} kg
(iii) (a) 1.2044×10^{22} protons (b) 2.015×10^{-5} kg
3.3 7,6: 8,8: 12,12: 30,26: 50, 38
3.4 (i) Cl (ii) U (iii) Be
3.5 5.17×10^{14} s^{-1}, $1.72 \times 10^{6} m^{-1}$
3.6 (i) 1.988×10^{-18} J (ii) 3.98×10^{-15} J
3.7 6.0×10^{-2} m, 5.0×10^{9} s^{-1} and 16.66 m^{-1}
3.8 2.012×10^{16} photons
3.9 (i) 4.97×10^{-19} J (3.10 eV); (ii) 0.97 eV (iii) 5.84×10^{5} m s^{-1}
3.10 494 kJ mol^{-1}
3.11 $7.18 \times 10^{19} s^{-1}$
3.12 $4.41 \times 10^{14} s^{-1}$, 2.91×10^{-19}J
3.13 486 nm
3.14 8.72×10^{-20}J
3.15 15 emmission lines
3.16 (i) 8.72×10^{-20}J (ii) 1.3225 nm
3.17 1.523×10^{6} m^{-1}
3.18 2.08×10^{-11} ergs, 956 Å
3.19 3647Å
3.20 3.55×10^{-11}m
3.21 8967Å
3.22 Na^{+}, Mg^{2+}, Ca^{2+}; Ar, S^{2-} and K^{+}
3.23 (i) (a) $1s^2$ (b) $1s^2\ 2s^2\ 2p^6$; (c) $1s^2 2s^2 2p^6$ (d) $1s^2 2s^2 2p^6$
3.24 n = 5
3.25 n = 3; $\ell = 2$; m_ℓ = -2, -1, 0, +1, +2 (any one value)
3.26 (i) 29 protons
3.27 1, 2, 15
3.28 (i)

ℓ	m_ℓ
0	0
1	-1,0,+1
2	-2,-1,0,+1,+2

(ii) $\ell = 2$; m_l=-2, -1,0,+1,+2
(iii) 2*s*, 2*p*
3.29 (a) 1*s*, (b) 3*p*, (c) 4*d* and (d) 4*f*
3.30 (a), (c) and (e) are not possible
3.31 (a) 16 electrons (b) 2 electrons
3.33 *n* = 2 to n = 1
3.34 8.72×10^{-18}J

UNIT 5

5.7 (a) 2.1×10^3J (b) 34g

5.8 6.6 min

5.9 (a) –890 kJ mol^{-1}

(b) –3351 kJ mol^{-1}

5.11 24.8, 28.3, 29.6, 31.0, 32.2 J $mol^{-1}K^{-1}$

Extrapolating gives about 33.5 J $mol^{-1}K^{-1}$ for Fr

5.12 ΔH = +513.4 J

5.13 ΔH = -1.662×10^3kJ mol^{-1}

5.14 $\Delta H_{O=O}$ = 422 kJ mol^{-1} of bonds

5.19 60.1 kJ

5.20 q = -5.28kJ

5.21 ΔH = -20.4 kJ and ΔU = -17.58 kJ

5.22 ΔH^o = -137 kJ mol^{-1}

UNIT 7

7.3 2.67×10^4

7.6 (i) 0.024 (ii) 6.4 (iii) 1.7×10^3

7.7 (a) 4.4×10^{-4} (b) 1.90

7.10 $[N_2] \approx 0.0482$ mol L^{-1}, $[O_2] \approx 0.0933$ mol L^{-1} and $[N_2O] \approx 6.6 \times 10^{-21}$ mol L^{-1}

7.11 0.0355 mol NO and 0.0178 mol Br_2

7.13 0.44

7.14 0.068 mol L^{-1} each of H_2 and I_2

7.15 (i) $Q_c = \dfrac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ (ii) 3.92

(iii) Value of Q_c is not equal to K_c, therefore, equilibrium is not attained.

7.16 0.02 mol L^{-1} for both

7.19 (b) 120.48

7.20 $(p_{H2})_{eq} = (p_{Br2})_{eq} = 2.5 \times 10^{-2}$ bar, $(p_{HBr})_{eq}$ = 10.0 bar

7.23 0.153

7.24 No, the reaction proceeds to form more product

7.25 3×10^{-4} mol L^{-1}

UNIT 8

8.1 NO^-_2, HCN, ClO_4^-, HF, H_2O, HCO_3^-, HS^-

8.2 BF_3, H^+, NH_4^+

8.3 F^- = 1.5×10^{-11}, $HCOO^-$ = 5.6×10^{-11}, CN^- = 2.08×10^{-6}

8.4 [Phenate ion] = 2.2×10^{-6}; pH = 5.65; $\alpha = 4.47 \times 10^{-5}$

8.5 $[HS^-] = 9.54 \times 10^{-5}$. In 0.1M HCl $[HS^-] = 9.1 \times 10^{-8}$M
$[S^{2-}] = 1.2 \times 10^{-13}$M; In 0.1M HCl $[S^{2-}] = 1.09 \times 10^{-19}$M

8.6 (a) 2.52 (b) 11.70 (c) 2.70 (d) 11.30

8.7 (a) 11.65 (b) 12.21 (c) 12.57 (d) 1.87

8.8 (a) 1.48×10^{-7}M (b) 0.063 (c) 4.17×10^{-8}M (d) 3.98×10^{-7}

8.9 (a) 1.5×10^{-7}M (b) 10^{-5}M (c) 6.31×10^{-5}M (d) 6.31×10^{-3}M
(e) 1.58×10^{-8}M

8.10 $[K^+] = [OH^-] = 0.05$M and $[H^+] = 2.0 \times 10^{-13}$M

8.11 $[Sr^{2+}] = 0.1581$ M; $[OH^-] = 0.3162$ and pH = 13.50

8.12 $\alpha = 1.63 \times 10^{-2}$; pH = 3.09; in presence of 0.01M HCl, $\alpha = 1.32 \times 10^{-3}$

8.13 $K_a = 2.09 \times 10^{-4}$ and degree of ionization = 0.0457

8.14 pH = 7.97 and degree of hydrolysis = 2.36×10^{-5}

8.15 $K_b = 1.5 \times 10^{-9}$.

8.16 NaCl, KBr solutions are neutral, NaCN, $NaNO_2$ and KF solutions are basic and NH_4NO_3 solution is acidic.

8.17 pH of acid solution = 1.94 and that of its salt solution = 7.94

8.18 pH = 6.81

8.19 the pH of solution at various stages of addition of KOH solution is 1.62, 2.34, 2.64, 3.34, 3.64, 7.0, 10.36 and 10.66. The suitable indicator is either phenolphthalein or thymolphthalein.

8.20 (a) 12.36 (b) 7.00 (c) 1.30

8.21 Neutral red or Bromothymol blue

8.22 Most suitable pH range is 9.5 to 11.5

8.23 Molar mass = 122 g mol^{-1}.

8.24 Silver chromate S = 0.65×10^{-4}M; Molarity of $Ag^+ = 1.30 \times 10^{-4}$M
Molarity of $CrO_4^{2-} = 0.65 \times 10^{-4}$M; Barium chromate S = 1.1×10^{-5}M; Molarity of Ba^{2+} and CrO_4^{2-} each is 1.1×10^{-5}M; Ferric Hydroxide S = 1.39×10^{-10}M;
Molarity of $Fe^{3+} = 1.39 \times 10^{-10}$M; Molarity of $[OH^-] = 4.17 \times 10^{-10}$M
Lead Chloride S = 1.59×10^{-2}M; Molarity of $Pb^{2+} = 1.59 \times 10^{-2}$M;
Molarity of $Cl^- = 3.18 \times 10^{-2}$M; Mercurous Iodide S = 2.24×10^{-10}M;
Molarity of $Hg_2^{2+} = 2.24 \times 10^{-10}$M and Molarity of $I^- = 4.48 \times 10^{-10}$M

8.25 Silver chromate is more soluble and the ratio of their molarities = 9.15

8.26 No precipitation

8.27 Silver benzoate is 3.317 times more soluble at lower pH.

8.28 The highest molarity for the solution is 5.02×10^{-9}M

8.29 2.46 litre of water

8.30 Precipitation will take place in ferrous sulphate and cadmium chloride solution.

UNIT 16

16.24 Mass of carbon dioxide formed = 0.5050g; mass of water formed = 0.0864g

16.25 Percentage of nitrogen in the compound = 56%

16.26 Molecular formula of the acid = $C_7H_6O_2$

16.27 A is $C_6H_5CH = CH_2$; B is C_6H_5CHO
C is addition polymer of A.

16.28 Molecular formula of the compound is C_2H_5Br

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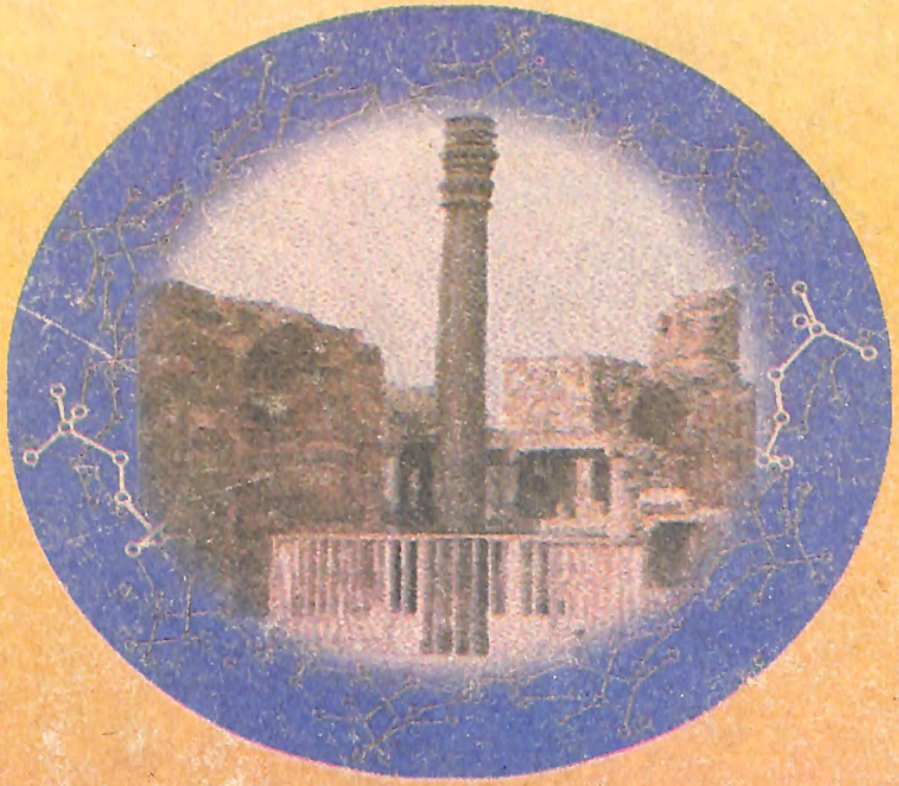

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एन सी ई आर टी
NCERT

राष्ट्रीय शैक्षिक अनुसंधान और प्रशिक्षण परिषद्
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